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Physico-chemical Laboratory Techniques in Organic and Biological Chemistry

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ИЗДАТЕЛЬСТВО
МИР

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ФИЗИКО-ХИМИЧЕСКИЕ МЕТОДЫ ИССЛЕДОВАНИЯ В ОРГАНИЧЕСКОЙ И БИОЛОГИЧЕСКОЙ ХИМИИ

ИЗДАТЕЛЬСТВО «ПРОСВЕЩЕНИЕ» МОСКВА

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TO THE READER

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Preface

Current teaching courses in organic and biological chemistry make an extensive use of the results obtained by means of the physico-chemical laboratory techniques. The data on molecular structures in organic chemistry are derived from such physical techniques as UV, IR, NMR, EPR and mass spectrometries, refractometry and so on. This book deals with the main molecular spectroscopic techniques (UV, IR, Raman and NMR spectroscopies) and the dipole moments technique.

The laboratory techniques described here have been selected according to their use in organic chemistry for determining structures and physico-chemical properties of synthesis products, and according to the availability of the respective research instruments in the university laboratories. Hence, the major portion of the book is given to the UV and IR spectroscopy techniques. A brief discussion covers the fundamentals of a technique and its applications, then follow laboratory exercises and problems for students. The final section presents problems involving combined use of several physical and chemical laboratory techniques. The problems have been selected to take into account the teaching programme of the secondary school in order to make it useful for the school teachers, and students preparing for that career.

Chapter 1

Electron Absorption Spectroscopy

Similar to other molecular spectroscopic techniques, the electron absorption spectroscopy has a wide variety of applications in studies of the properties and structures of organic compounds, such as determination of structure and identification of a compound, evaluation of the purity of a product, analysis of kinetics and mechanisms of chemical reactions, quantitative determinations for simple and multicomponent systems, accurate measurements of the dissociation constants for acids and bases, analysis of the complexing processes (particularly those of the donor-acceptor nature), etc.

FUNDAMENTALS OF ELECTRON SPECTRA THEORY

Stationary States. Bohr's Postulates

The molecular spectroscopy (for the electronic, vibrational, rotational and other levels) studies the interactions between the electromagnetic radiation and the matter, and its theory stems from two concepts postulated by Bohr.

According to Bohr's postulates, atoms (or molecules) can exist without changing their energy, that is, without emission or absorption of radiation, only at certain stable states. The energies of these states comprise a discrete series $E_1, E_2, \ldots, E_x$ known as the system of energy lev-

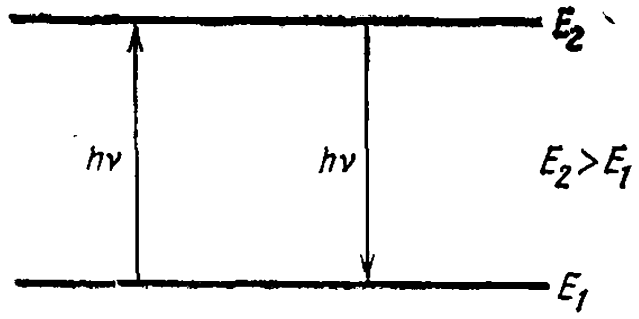


Fig. 1.
Energy levels according to Bohr's postulates (the downward arrow denotes transition with emission, the upward arrow denotes transition with absorption).

els (Fig. 1). When an atom absorbs or emits some energy, ΔE, it jumps from one stable state to another one. The energy $h\nu$ of the absorbed or emitted quantum is equal to the variation ΔE of the system's energy. Hence, absorption or emission of radiation can occur only if the energy of the absorbed (emitted) quantum is equal to the difference between two energy levels:

$$\Delta E = E_2 - E_1 = h\nu = \frac{hc}{\lambda} \qquad (1)$$

and

$$\nu = \frac{E_2 - E_1}{h} \qquad (2)$$

Here c is the velocity of light, λ and ν are the wavelength and frequency of radiation, and h is Planck's constant.

Substitution of numerical values for h and c into eq. (1) yields

$$\Delta E \approx 120\,000 \frac{1}{\lambda} = 120\,000\bar{\nu}$$

Here ΔE is expressed in kilojoules per mole and λ in nanometers; $1/\lambda = \bar{\nu}$ (cm^{-1}) is the wave number and in spectroscopy it is often referred to as the frequency. There is a linear relationship between the wave number and the radiation energy: 1 cm^{-1} corresponds to 11.96 J/mole or $1.24 \cdot 10^{-4}$ eV.

Eq. (1) can yield directly the frequency ν of radiation.

Electromagnetic Radiation Energies and Types of Molecular Spectra

The molecular spectra have a considerably more complex structure than the atomic ones because in molecules, apart from the electronic degrees of freedom, there are also the rotational and vibrational degrees of freedom of the nuclei. The total energy E of a molecule can be expressed approximately (without taking into account the interaction between various types of motion) as a sum of the electronic, E_{el}, rotational, E_{rot}, and vibrational, E_{vib}, energies:

$$E = E_{el} + E_{vib} + E_{rot} \tag{3}$$

All the three types of molecular energy are quantized, that is, they can have only certain values proportional to Planck's constant, the intermediate energy values being forbidden. Theoretical and experimental results yield the following relationship between the above three types of energy:

$$E_{el} : E_{vib} : E_{rot} = 1 : \sqrt{\frac{m}{M}} : \frac{m}{M} \tag{4}$$

Here m is the mass of the electron and M is the mass of the nucleus. For instance, for the hydrogen molecule ($M \approx \approx 900\ m$), Eq. (4) yields

$$E_{el} : E_{vib} : E_{rot} = 1 : 1/30 : 1/900$$

The experimental results for the hydrogen molecule are: $E_{el} \approx 10$ eV, $E_{vib} \approx 0.5$ eV and $E_{rot} \approx 0.015$ eV, so that $E_{el} : E_{vib} : E_{rot} = 1 : 1/20 : 1/700$.

A considerable difference is thus apparent between the electronic, vibrational and rotational energies:

$$E_{el} \gg E_{vib} \gg E_{rot} \tag{5}$$

so that they correspond to different spectral ranges (Fig. 2).

When a molecule absorbs small amounts of energy (hundreds of joules per mole), it is excited to a higher rotational state while its vibrational and, of course, electron states remain unaltered. These energies correspond to absorption (emission) of the radiation with the wavelengths of 1-0.1 mm or more, that is, the wave numbers of 10-100 cm^{-1} or less. Thus, the purely rotational spectrum is found at the far infrared range or even at the radio-frequency (r.f.) range. At higher radiation energies the vibrational levels are excited; they correspond to the wavelengths of 2.5-100 μm, hence to wave numbers of 100-4000 cm^{-1}. Obviously, excitation of the vibrational levels entails excitation of the rotational levels, so that the resulting spectrum is a vibrational-rotational one. This spectrum is in the infrared range closer to the visible range. Excitation of the electronic levels occurs, typically, at much higher energies (of the order of hundreds of kilojoules per mole) corresponding to the visible and ultraviolet ranges of the spectrum (100-800 nm). At such radiation energies the vibrational and rotational spectra are also excited.

The electronic spectral range of Fig. 2 is shown in more detail in Fig. 3. The molecular electronic spectral range lies between $\sim 10^5$ cm^{-1} (100 nm) and $\sim 10^4$ cm^{-1} (1000 nm) and is classified into two ranges—the visible range between 400 and 1000 nm and the ultraviolet range between 400 and

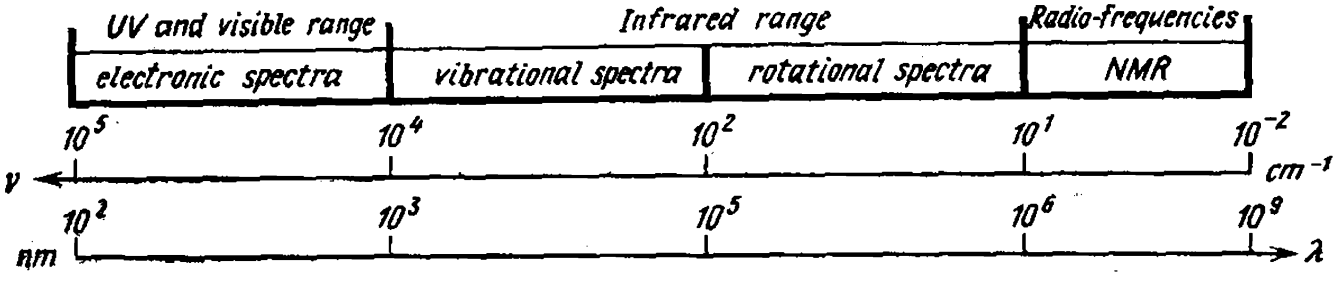


Fig. 2.
Radiation wavelengths and energy scale for rotational, vibrational and electron transitions.

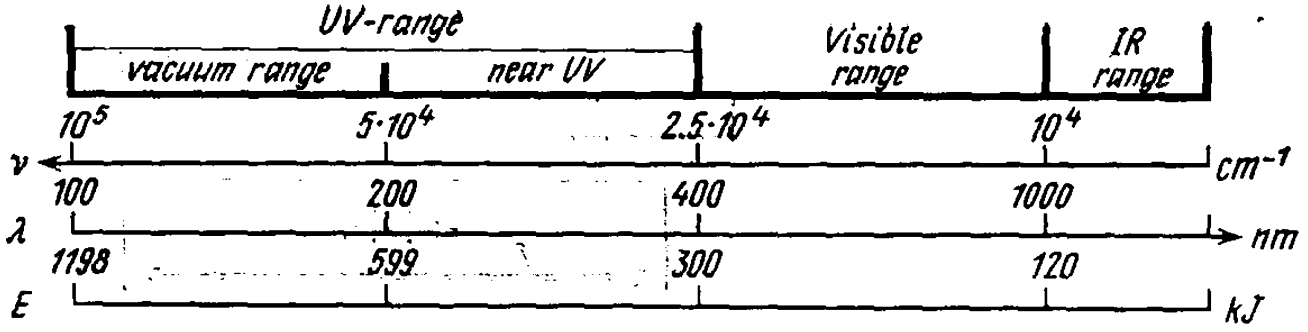


Fig. 3.
Radiation wavelengths and energy scale for electron transitions.

100 nm. This classification stems from a purely physiological fact that the human eye cannot see the ultraviolet light. In its turn, the ultraviolet range is divided into two subranges—the near subrange between 200 and 400 nm and the far, or vacuum, subrange between 100 and 200 nm. The latter is called the vacuum subrange because the air has the absorption bands in this subrange so that the spectral studies should be carried out in an evacuated spectrometer.

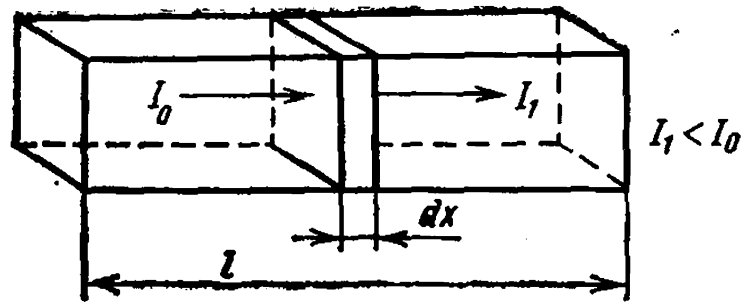
The Fundamental Law of Light Absorption (the Beer-Lambert-Bouguer Law)

The light absorption is the reduction of the light flux in a material, owing to conversion of the radiation energy into the internal energy of the material. The absorption of light should be distinguished from the scattering of light when the light flux along the initial direction is reduced owing to deflection of a fraction of the flux.

For the optical spectra (electronic, vibrational, rotational) there is a general radiation absorption law relating the absorbed radiation to the amount of the absorbing material.

Let us consider a thin layer of a material absorbing light (Fig. 4). The light flux I_0 incident on this layer is partially absorbed there so that the light flux leaving the layer is

Fig. 4.
Illustration to Beer's law.



$I_0 - dI$. Bouguer and Lambert have found that the light absorbed in the homogeneous material, dI, is proportional to the thickness, dx, of the absorbing layer. According to Beer's law, dI is proportional to the number of the absorbing particles in the layer dx, that is, to their concentration:

$$\frac{dI}{I} = -\varepsilon' \cdot c \cdot dx \tag{6}$$

Here c is the concentration of the absorbing particles (in moles per litre), and ε' is the probability of absorption by particles with unit concentration per unit incident flux. Integration of eq. (6) over x from 0 to l yields

$$\int_{I_0}^{I_1} \frac{dI}{I} = -\varepsilon' \cdot c \cdot \int_0^l dx \tag{7}$$

or

$$\ln \frac{I_1}{I_0} = -\varepsilon' \cdot c \cdot l \tag{8}$$

Introducing common logarithms, we obtain

$$-\log \frac{I_1}{I_0} = \varepsilon \cdot c \cdot l \quad (\varepsilon = 2.3 \cdot \varepsilon') \tag{9}$$

The parameter $-\log (I_1/I_0) = D$ is known as the optical density and the parameter $T = (I_1/I_0)\,100$ is known as the percent transmittance ($D = -\log T$). These parameters can be found experimentally.

Hence we obtain

$$D = \varepsilon \cdot c \cdot l \tag{10}$$

where ε is the molar extinction coefficient. Most spectrophotometric studies in chemistry make use of eq. (10) (deviations from eq. (10) and their causes are discussed below).

Energy Levels of Diatomic Molecules

The electron energy level of a molecule under normal conditions is known as the ground state (E_0), and the electronic levels with the higher energies are called the first, second and so on, excited states (E_1, E_2, . . .).

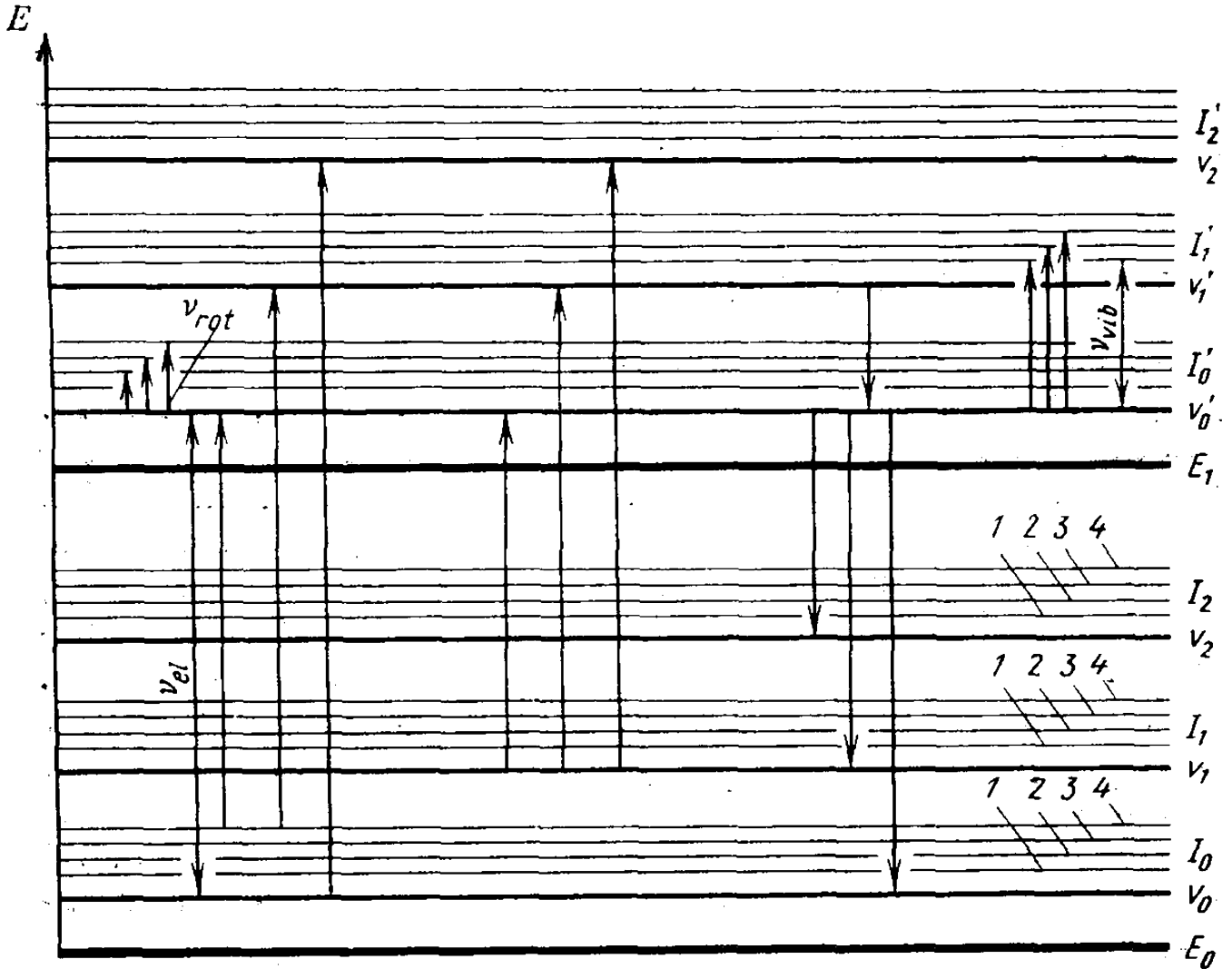


Fig. 5.
Electron, vibrational and rotational levels and transitions.

Each electronic state, E_0 for example, has its own system of vibrational levels consisting of one ground level (v_0) and several excited levels (v_1, v_2, . . .); in its turn, each vibrational state (for instance, v_1) has its own system of rotational levels consisting of one ground level (I_{11}) and several excited levels (I_{12}, I_{13}, I_{14}, . . .). Fig. 5 presents a schematic diagram of two electron levels (E_0 and E_1) of a molecule (actually, there are more than two levels), and the respective vibrational and rotational levels. It can be seen from the diagram that the lowest electron level to be occupied is the ground vibrational level v_0 rather than the purely electron level E_0. The explanation is that in the diatomic molecule (or a polyatomic molecule) there always occur some vibrations even at the absolute zero so that the electron cannot occupy the ground level E_0.

The Frank-Condon Principle

An excited state of a molecule differs significantly in the properties and structure from the ground state, which for the diatomic molecule implies a change in the shape of the potential function $E(r)$ (Fig. 6). For instance, excitation can lead to an increase or (more commonly) a decrease in the dissociation energy D, a decrease or (more commonly) an increase in the equilibrium distance, r, between the nuclei or, finally, the excited state can prove to be unstable.

The main problem encountered in analysis of a molecular electron spectrum can be formulated as follows. Assume that a radiation quantum $h\nu$ is absorbed by a molecule which is at the ground electron level and a vibrational level v. At what vibrational level will the molecule be found after absorption of a radiation quantum, or at which point of the potential curve can we find it with the highest probability? The answer is provided by the Frank-Condon principle which is based on the extremely fruitful idea that the electron

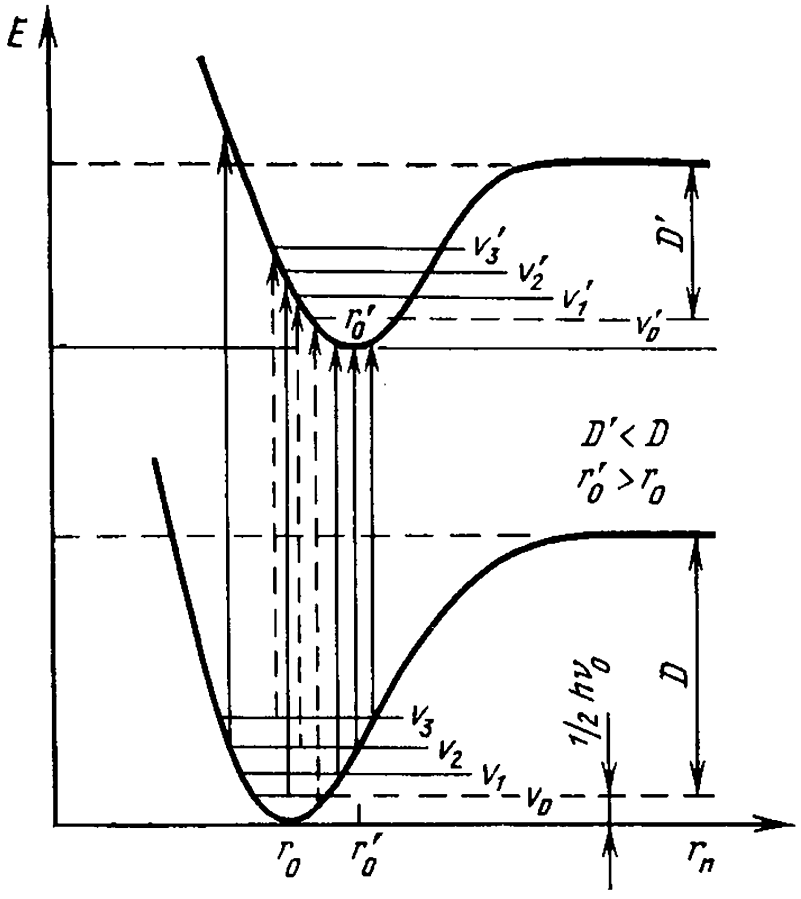


Fig. 6.
The most probable electron-vibrational transitions according to the Frank-Condon principle.

transition is so fast (the characteristic time of 10^{-14}-10^{-15} s) as compared to the vibrational transition (the vibration period of the nuclei is 10^{-12}-10^{-13} s) that while it occurs neither the relative positions of the nuclei nor their velocities change. In other words, the nuclei are at fixed positions during the electron transition and the excited molecule has the same distance r between the nuclei as the molecule at the ground level. Hence, we can find the vibrational states of the excited molecule as the points on the potential curve for the excited molecule (Fig. 6, upper curve) where it is intersected by the vertical lines passing through the points of the most probable states at the potential curve for the ground state of the molecule (that is, mostly the points where

the velocities of the nuclei are zero as their direction of motion is reversed). The respective transitions (shown by solid arrows) give the bands of the highest intensity in the spectrum while the transitions shown by the dashed arrows have low probabilities (or do not occur at all).

The Frank-Condon principle and Bohr's postulates are the fundamental concepts of the theory of molecular spectroscopy.

Electron Spectra of Polyatomic Molecules

The case of diatomic molecules has been discussed because it is easier to analyze due to simple chemical bonding. However, the main objects of study in chemistry and biology are the polyatomic molecules. We shall consider here only a part of the molecular electrons, namely the valence (outer) electrons, which are involved in chemical bonding and determine the chemical properties of the molecules (we include here also the unshared electron pairs of the heteroatoms).

Classification of Electron Transitions. The electron transitions in molecules are classified according to the types of the valence electrons in them. The electrons of the single bonds are known as the σ-electrons and the electrons of the double (and triple) bonds are called the π-electrons. Moreover, unpaired electrons (or *n*-electrons) can exist in molecules containing such atoms as oxygen, nitrogen, etc. The electron distribution in molecules is described by the σ-, π- and *n*-orbitals which are typically occupied by electrons when the molecule is in the ground state. When a molecule is excited by a radiation quantum the electrons can be excited from a bonding (σ, π) or nonbonding (*n*) orbital to a higher-energy antibonding orbital (σ*, π*) which is vacant in the ground state.

Fig. 7.
Various electron levels and transitions between them.

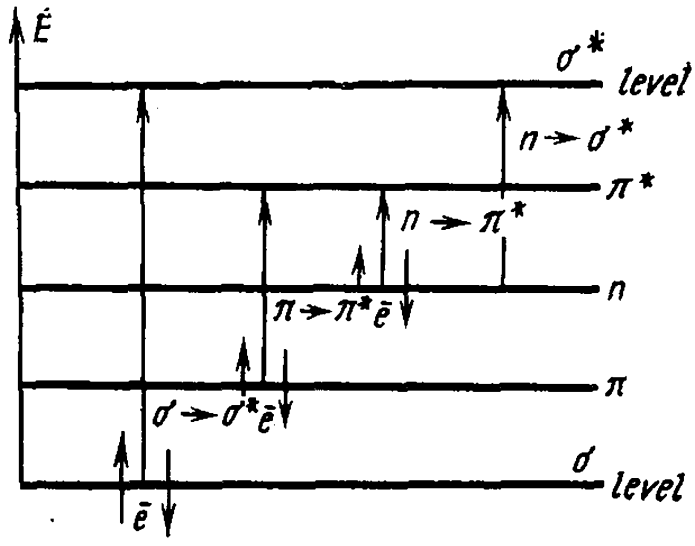
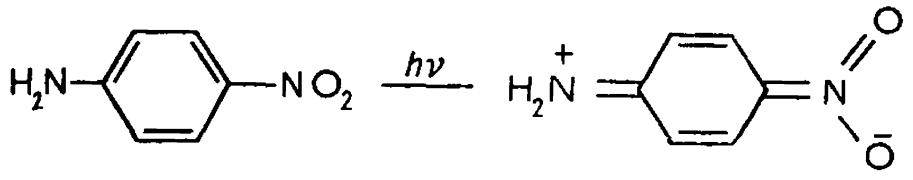


Fig. 7 shows the existing types of transitions and the energy states of the n-, π- and σ-electrons. The diagram illustrates relative arrangement of the spectral bands corresponding to the above transitions.

The $\sigma \rightarrow \sigma^*$ transitions correspond to the highest excitation energy since the σ-bond is the strongest one. These transitions are typical of the saturated hydrocarbons, and their characteristic bands appear in the "vacuum" ultraviolet region at $\lambda < 200$ nm. The $\pi \rightarrow \pi^*$ transitions occur at much lower energies, they are typical of unsaturated compounds and correspond to the near ultraviolet and visible ranges. The transitions $\pi \rightarrow \pi^*$ and $\sigma \rightarrow \sigma^*$ are known also as the $N \rightarrow V$ transitions. The transitions $n \rightarrow \sigma^*$ (for instance, in CH_3NH_2) and $n \rightarrow \pi^*$ (in ketones) occur from the "atomic" (nonbonding) orbital of the ground state to the molecular antibonding orbitals σ^* and π^*. They are sometimes referred to as the $N \rightarrow Q$ transitions. Typically, the n-levels are higher than the π-levels so that the $n \rightarrow \pi^*$ band in the absorption spectrum has the largest wavelength (the lowest energy).

A fairly recent result is that some intense spectral bands are due to the intramolecular charge transfer so that they should be subsumed into a special group. In these transitions the electron density within a molecule is shifted from

the electron-donor group to the electron-acceptor group (this effect must be distinguished from the charge transfer between different molecules). This is illustrated by the long-wavelength absorption band of nitrobenzene and its *para*-derivatives:



A suggested criterion for assignment of the bands to the charge-transfer transitions is the correlation between the transition energy $h\nu$ and the difference between the ionization energy I_D of the donor and the electron affinity energy E_A of the acceptor:

$$h\nu \approx I_D - E_A \qquad (11)$$

Fig. 8 illustrates transitions in the simple case of formic acid. In the ground state the higher orbitals of the OH and C=O groups are occupied by electrons (Fig. 8, *1*). The lower vacant orbital belongs to the carbonyl group (since this is a π-orbital). One of the electrons of the OH group can be excited to this orbital (Fig. 8, *2*); it is just this process that is known as the charge-transfer transition. The charge-transfer spectral lines are among those with the highest intensities.

Intensities of the Electron Transitions and the Difference Between Them. The primary difference between the $n \rightarrow \pi^*$

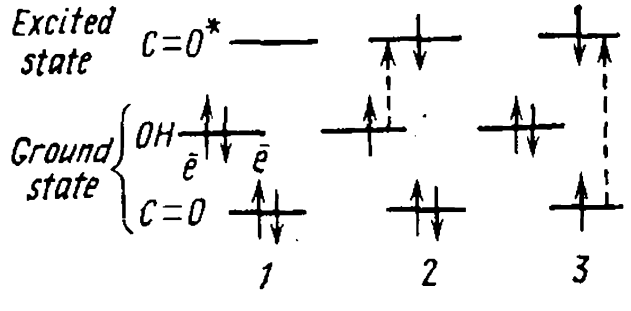


Fig. 8.
Electronic states in formic acid HCOOH. *1*—ground state, *2*—intramolecular charge transfer with electronic excitation, *3*—local excitation at the carbonyl group.

transitions and the $\pi \rightarrow \pi^*$ (and charge-transfer) transitions lies in the intensities. While the molar extinction coefficient ε_{max} at the band maximum is 10 000 or more for the permitted $\pi \rightarrow \pi^*$ transitions and from about 200 to a few thousand for the forbidden transitions, for the $n \rightarrow \pi^*$ bands this coefficient varies from a few units to a few hundreds. Many authors attribute such low intensities to the fact that the $n \rightarrow \pi^*$ transitions are forbidden owing to the symmetry conditions.

A useful experimental criterion for assigning a band to the $\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$ transition is the shift of the absorption maximum on increasing the solvent polarity (the MacConnel rule) (using, instead of nonpolar solvents such as heptane or carbon tetrachloride, the polar ones such as water or alcohol): the $\pi \rightarrow \pi^*$ absorption moves to longer wavelength (a "red" or bathochromic shift) whereas the $n \rightarrow \pi^*$ band usually moves to shorter wavelength (a "blue" or hypsochromic shift).

The most reliable assignment of a band to a transition involving antibonding orbitals ($n \rightarrow \pi^*$) can be based on disappearance of the band in acidic mediums. This is due to protonation of the unshared pair of n-electrons so that the orbital is no longer antibonding and the transition does not occur at all.

Continuous Spectra of Polyatomic Molecules. The larger is the number of atoms in a molecule the higher is the density (the number) of the vibrational levels. Closely spaced vibrational levels affect each other, that is, they can no longer be treated as the noninteracting levels. Hence, increasing the number of atoms in the molecule results in a gradual disappearance of the bands corresponding to individual electron vibrational transitions in the electron spectrum. For a molecule with a small number of atoms (3, 4, or 5) the electron spectrum has a structure similar to the band structure of the spectrum of diatomic molecules (Fig. 9, *2*). A further increase in the number of atoms in a

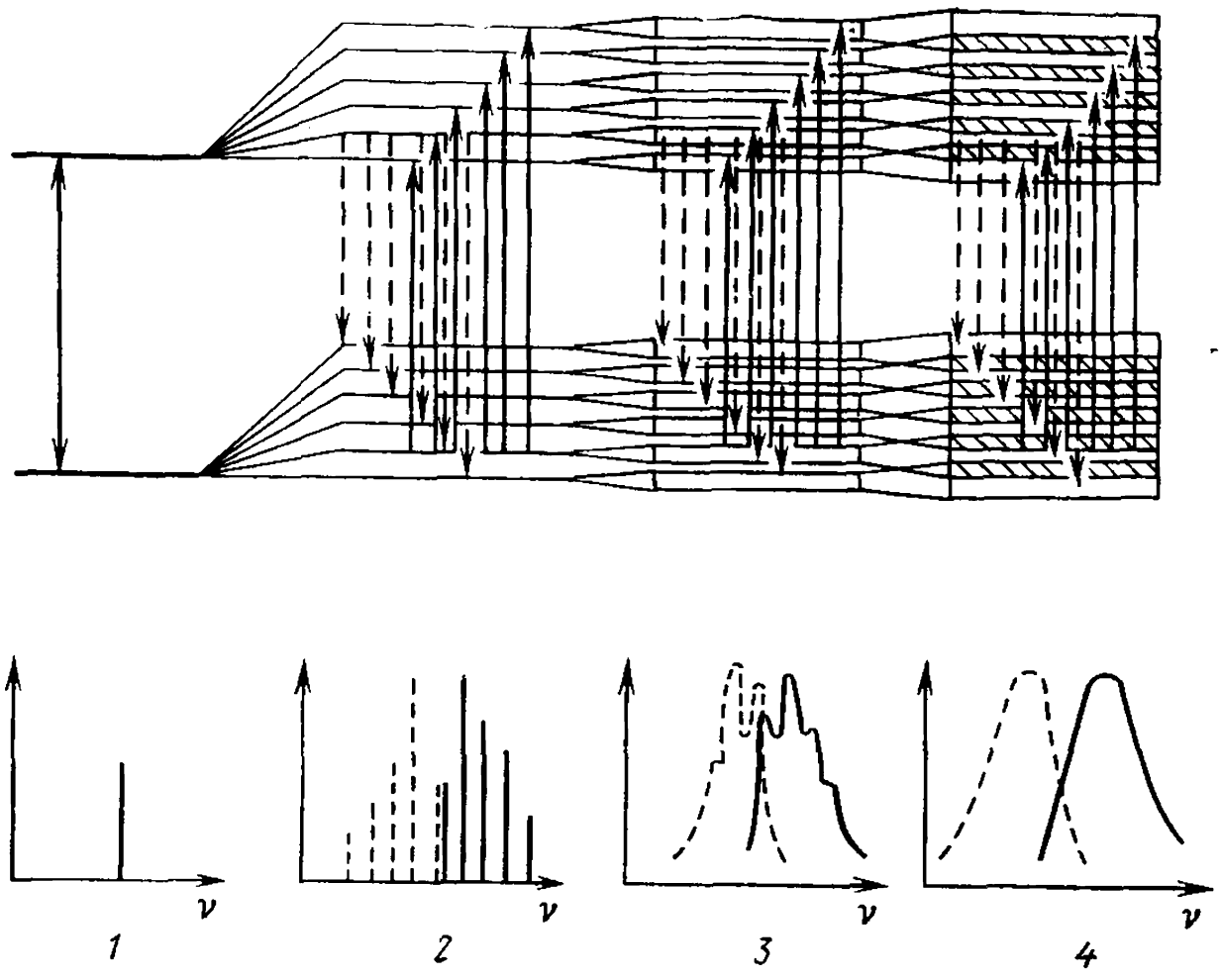


Fig. 9.
Transition from the structured to continuous spectra. Electron levels and spectra: *1*—atoms, *2*—molecules with weak interaction, *3*—molecules with intermediate interaction, *4*—molecules with strong interaction between vibrations.

molecule results in spreading out of the vibrational maximums in the electron spectra. Each electron transition produces a wide absorption band with more or less significant traces of the vibrational structure, in the form of small secondary maximums or minimums (Fig. 9, *3*). For the molecules with still larger number of atoms (and this is typical of organic chemistry) even these remaining traces of the vibrational structure disappear and the spectra consist of wide structureless electronic bands with single maximums (Fig. 9, *4*). Under such circumstances many specific features

of the electron spectrum are lost (in contrast to the IR spectrum); various complex molecules prove to have similar bands differing mainly in their frequency ranges. Fig. 9 illustrates variation of the vibrational levels and the electron vibrational spectrum with the increase in the number of atoms in a molecule.

Thus, the wide structureless bands have been found to be due primarily to the intramolecular (rather than intermolecular!) processes, namely the extremely strong interaction between vibrations. Therefore, no simple physical meaning can be ascribed to the peak frequency of an electronic band which has a complex dependence on the distribution of probabilities for individual transitions, on the level densities in the electronic states, etc. Most experimental studies have been concerned with just these maximums of the absorption (emission) bands but interpretation of these results is frequently hindered by the lack of any clear understanding of their physical meaning. A much more reasonable approach is to consider the frequency ν_e of a purely electron transition (Fig. 10), that is, a transition between the levels with the zero vibrational energy in both states (the transition $v_0 \rightarrow v_0'$ in Fig. 5). Unfortunately, it

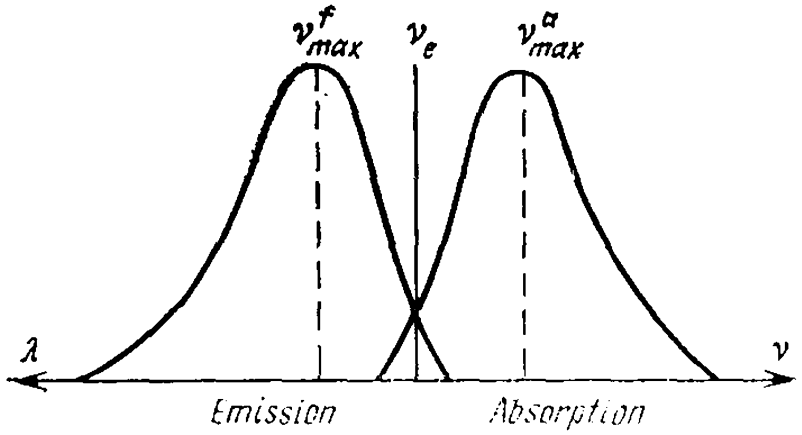


Fig. 10.
The positions of the absorption and emission bands for complex molecules: ν^a_{max}—the peak of the absorption band, ν^f_{max}—the peak of the emission band, ν_e—the peak of the purely electronic transition (crossover of bands).

is rather hard to determine ν_e for the complex molecules so that below we shall interpret the experimental results only using the peak frequency of the electronic absorption band ν^a_{max} (Fig. 10).

Effect of Intermolecular Interactions on the Electron Spectra (Effect of the Solvent)

When a molecule goes over from the gas phase to a condensed phase all the parameters of the absorption spectrum are generally changed (the positions, intensities and shapes of the absorption bands). The factors which can produce these changes are rather complicated. Therefore, here we shall limit ourselves to analyzing the effect of the Van der Waals forces (which have primarily inductive and orientational character) on the position of the absorption band peak. This effect can be satisfactorily represented by the highly simplified scheme of Fig. 11.

We have repeatedly noted that the frequency (wavelength) of an electron transition is determined by the energy difference between the ground state and the excited state. The frequency ν_0 in Fig. 11 describes the transition in the gaseous phase (where there are no intermolecular interactions). If this molecule is transferred to a condensed phase (solution) its interaction with the solvent molecules results in its stabilization (that is, both electron levels of the molecule are lowered). Here the larger the dipole moment of the molecule (μ) the stronger the solvate complex and the higher is the stabilization energy. Since the dipole moments of

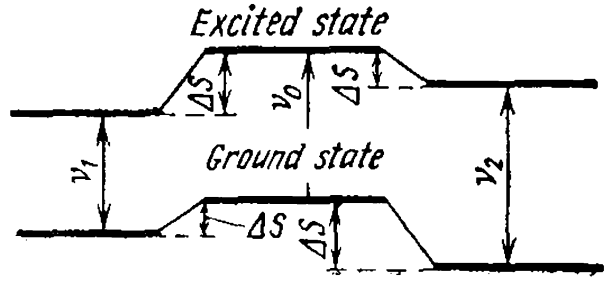


Fig. 11.
Effect of the solvent on the position of electron levels (for simplicity vibrational and rotational levels are neglected).

the ground (μ_g) and the excited (μ_e) states generally differ, their stabilization energies (ΔS) are rather different; two cases are possible here (Fig. 11):

(1) The dipole moment of the ground state is considerably larger than that of the excited state ($\mu_g \gg \mu_e$). Clearly, stabilization of the molecule excited by absorption of a quantum is weaker than the stabilization of the non-excited molecule ($\Delta S_g > \Delta S_e$). This results in a high-frequency (short-wavelength) shift of the absorption band peak ν_2 due to dissolving ($\nu_2 > \nu_0$ and $\lambda_2 < \lambda_0$).

(2) The dipole moment of the excited molecule is considerably higher than that of the ground state ($\mu_e \gg \mu_g$). The result is the reverse of (1), viz. the stabilization energy of the ground state is lower than that of the excited state and the absorption band peak ν_1 is shifted to the lower frequencies (higher wavelengths) ($\nu_1 < \nu_0$ and $\lambda_1 > \lambda_0$).

Fig. 11 illustrates a possible cause of the shift of $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions with increasing polarity of the solvent (p. 71): (a) for the $n \rightarrow \pi^*$ transition in formaldehyde, $H_2C{=}O$, the unshared electron pair localized near the oxygen atom in the nonexcited molecule is transferred to the antibonding π-orbital whose centre of gravity is between the oxygen and carbon atoms so that the electron density is shifted from O to C (in the ground state the opposite shift occurs—from C to O) and the dipole moment of the molecule is reduced ($\mu_g = 2.5$ Debyes $> \mu_e = 1.5$ Debyes) shifting the absorption band to the higher frequency (case 1); (b) the molecule $H_2N{-}C_6H_4{-}C_6H_4{-}NO_2$ ($\mu_g = 6.4$ Debyes $< \mu_e = 18$ Debyes) exhibits a low-frequency shift (case 2).

Electron Spectra of the Main Classes of Organic Chemistry

Alkanes and Cycloalkanes. The saturated hydrocarbons have only single bonds involving σ-electrons so that only the $\sigma \rightarrow \sigma^*$ transitions can occur in them. The respective bands

are found in the vacuum ultraviolet range, e.g. λ_{max} = = 125 nm for methane, and λ_{max} = 135 nm for ethane. The ethane molecule is excited at the C—C bond, and the methane molecule at the C—H bonds. The strength of the C—C bond is lower so that the absorption band of ethane is found at longer wavelengths. The absorption band of cyclopropane lies at about 190 nm since the three-member ring is to a certain extent unsaturated.

The spectra of saturated compounds containing heteroatoms with unshared electron pairs exhibit, apart from $\sigma \rightarrow \sigma^*$ absorption bands, the $n \rightarrow \sigma^*$ absorption bands at longer wavelengths (Table 1).

TABLE 1

ABSORPTION BANDS OF SATURATED COMPOUNDS WITH HETEROATOMS

Compound	Absorption bands			
	$\sigma \rightarrow \sigma^*$		$n \rightarrow \sigma^*$	
	λ (nm)	log ε	λ (nm)	log ε
CH_3OH	150	—	183	2.18
$(CH_3)_2O$	150	—	184	3.0
C_2H_5SH	192	3.9	225	2.2
$(CH_3)_2S$	210	2.5	229	2.2
CH_3NH_2	173	—	213	2.8
$(C_2H_5)_3N$	199	—	227	2.9
CH_3Cl	150	—	173	2.3
CH_3Br	—	—	204	2.3
CH_3I	150-210	—	258	3.5

The mobility of the unshared electron pair increases in the heteroatom series Cl < O < N < I so that the energy of the $n \rightarrow \pi^*$ transition decreases (the band with the largest wavelength (258 nm) is found in the spectrum of methyl iodide).

Unsaturated Compounds. The ultraviolet spectra of alkenes are determined primarily by the π-electrons which are excited at lower energies than the σ-electrons. The respective $\pi \rightarrow \pi^*$ bands lie in the 163-195 nm range. The ethylene absorption band is at 163 nm. The alkyl-substituted ethylenes have wide high-intensity bands ($\varepsilon \approx 10\,000$) at 173-190 nm (Table 2). Positions of the bands depend on the number of the alkyl groups and the nature of the substituents (*cis*, *trans*) at the double bond (Table 2).

TABLE 2

ABSORPTION BANDS OF NONSATURATED HYDROCARBONS

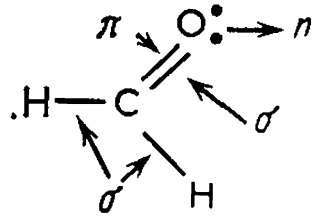
Compound	λ (nm)	log ε	Compound	λ (nm)	log ε
$CH_2=CH_2$	163	—	*cis*-$CH_3CH=CHCH_3$	175	4.3
$CH_3CH=CH_2$	173	4.2	*trans*-$CH_3CH=CHCH_3$	177	4.1
$C_2H_5CH=CH_2$	175	4.2	*cis*-$C_2H_5CH=CHCH_3$	177	4.3
$C_3H_7CH=CH_2$	177	4.2	*trans*-$C_2H_5CH=CHCH_3$	181	4.2
$C_4H_9CH=CH_2$	179	4.0			

The $\pi \rightarrow \pi^*$ band of acetylene lies at 173 nm; for the compounds of the $RC \equiv CH$ type the band peak is found at 186.5 nm and for the $RC \equiv CR$ type at 190.5 nm.

The presence of the halogen atom is evidenced in the spectra of alkenyl halides by the long-wavelength shift of the $\pi \rightarrow \pi^*$ band due to the resonance effect: ethylene—163 nm, chloroethylene—185 nm, 1,1-dichloroethylene—192 nm, trichloroethylene—196 nm, and tetrachloroethylene—197 nm.

The Carbonyl Compounds. The carbonyl group is found in aldehydes, ketones and in carboxylic acids and their derivatives. These compounds contain heteroatoms linked with multiple bonds. The following four types of electron transitions can occur in these compounds (p. 18): $\sigma \rightarrow \sigma^*$, $\pi \rightarrow$

$\rightarrow \pi^*$, $n \rightarrow \sigma^*$, and $n \rightarrow \pi^*$. All these types of transitions can be found in formaldehyde:



The most typical for carbonyl compounds is the absorption band of the $n \rightarrow \pi^*$ transition. This transition usually requires the smallest energy so that the band has the largest wavelength lying (for aldehydes and ketones) at the 270-300 nm region (about 35 000 cm^{-1}) which can be analyzed with the conventional spectrophotometers. These bands (as all $n \rightarrow \pi^*$ bands) are distinguished by low intensities ($\varepsilon \approx$ 10-50) and by shifting to shorter wavelengths with increasing polarity of the solvent, in striking contrast to $\pi \rightarrow \pi^*$ bands (Table 3).

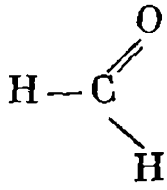
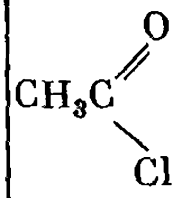
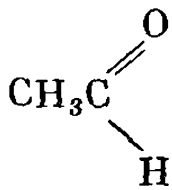
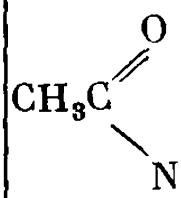
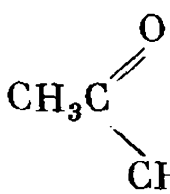
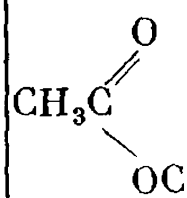
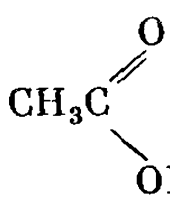
Fatty acids exhibit weak peaks at 205 nm ($\varepsilon \approx 50$). The spectra of esters do not differ much from the spectra of respective acids.

The absorption bands of both anhydrides and chloroanhydrides of various acids lie at longer wavelengths. For instance, the absorption band of acetyl chloride is at 235 nm ($\varepsilon = 53$). The differences between the spectra of acids and their derivatives and the spectra of aldehydes and ketones are attributed to the effects on the carbonyl group produced by the substituents with unshared electron pairs, including the inductive and resonance effects.

The resonance effect results in a rise in the energies of the levels π (to a larger extent) and π^*. Hence, the $\pi \rightarrow \pi^*$ band is shifted to longer wavelengths (the energy difference between the levels is reduced). But the $n \rightarrow \pi^*$ band is shifted to a shorter wavelength since the n level is not affected by the resonance interaction while the π^* level is raised

TABLE 3

$n \rightarrow \pi^*$ ABSORPTION BANDS OF CARBONYL COMPOUNDS

Compound	Solvent	λ_{max}	ε_{max}	Compound	Solvent	λ_{max}	ε_{max}
	Isooctane	310	15		Hexane	235	53
	Hexane	293	12		Water	214	—
	Hexane	279	15		Water	204	60
	Alcohol	204	41				

(the energy difference between the levels increases). The resonance effect of the CH_3 group can account for the shift to shorter wavelengths of the $n \rightarrow \pi^*$ band in the formaldehyde-acetyl aldehyde-acetone series.

All the atoms with the unshared electron pairs have a higher electronegativity than carbon. Owing to this reason the unshared pairs of the carbonyl oxygen become more strongly bound when an electronegative substituent is introduced into the molecule; this means that the energy of the n level is decreased by the inductive effect. The π level is also affected by the inductive effect but to a lesser degree. Therefore, a combined inductive and resonance effect results

in a considerable shift of the $n \rightarrow \pi^*$ band to shorter wavelength when we go over from ketones and aldehydes to acids, esters and amides (as compared to the formaldehyde-acetaldehyde-acetone series).

Nitrogen Compounds. Amines are the simplest nitrogen compounds. Their spectra have two absorption bands due to the $n \rightarrow \sigma^*$ transitions. These bands are shifted to longer wavelengths with increasing number of substituents: methylamine—173 and 215 nm, dimethylamine—190 and 220 nm, and trimethylamine—199 and 227 nm. Addition of the amino group to the ethylene group results in a bathochromic shift of 40-90 nm and an increase in the intensity up to 20 000.

The compounds with multiple bonds of the nitrogen atom exhibit $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ bands. For instance, fatty azomethines of the $R_3C{-}CH{=}NR$ type have a $n \rightarrow \pi^*$ band at 230-250 nm ($\varepsilon = 100$) and a $\pi \rightarrow \pi^*$ band at 190 nm. The systems $N{=}C{-}C{=}C$ and $N{=}C{-}C{=}N$ have a high intensity band ($\varepsilon \approx 20\,000$) at 220 nm which is found at 210 nm for the systems $C{=}N{-}N{=}C$.

The spectra of nitriles ($C{\equiv}N$) are similar to those of the respective acetylene compounds but the bands are shifted to shorter wavelengths (100-180 nm). For instance, the spectrum of acetonitrile has a band at 129 nm which is due to excitation of the π electrons of the triple bond. The nitrogen compounds with the $N{=}N$ group have low-intensity bands in the visible (330-350 nm, $\varepsilon \approx$ 20-400) and ultraviolet (200 nm, $\varepsilon \approx 1000$) ranges.

Nitro-Compounds. Nitroparaffins have two absorption bands—a $\pi \rightarrow \pi^*$ band at about 50 000 cm^{-1} (200 nm, $\varepsilon \approx 50\,000$) and a $n \rightarrow \pi^*$ band at 36 000 cm^{-1} (270 nm, $\varepsilon =$ 20-40). In nitro olefines the $\pi \rightarrow \pi^*$ band is found in the 220-250 nm range ($\varepsilon \approx 10\,000$). In nitrobenzene the $n \rightarrow \pi^*$ band lies at 330 nm ($\varepsilon = 125$). The band at 260 nm ($\varepsilon = 8000$) is produced by the transition with the charge transfer from the benzene ring to the nitro group.

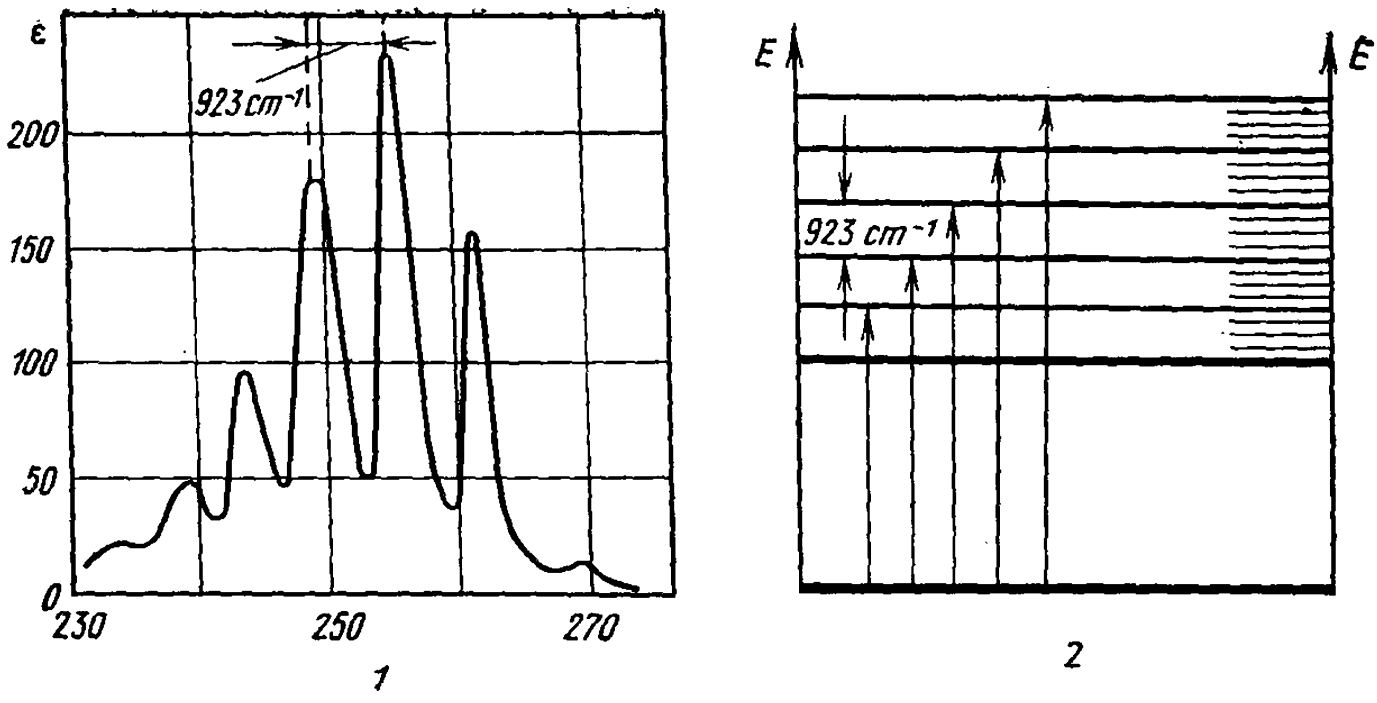
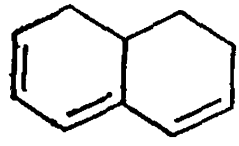


Fig. 12.
1—the long-wavelength band of the benzene spectrum; *2*—vibrational levels in the first excited electron state.

Aromatic Compounds. The long-wavelength benzene spectrum contains three bands: (1) the band at 180 nm is attributed to the allowed $\pi \rightarrow \pi^*$ transition ($\varepsilon \approx 60\,000$); (2) the band at 203 nm ($\varepsilon \approx 8000$) is assigned to a symmetry-forbidden transition; (3) the band which lies at 230-260 nm with the peak at 256 nm ($\varepsilon \approx 200$) and has a marked vibrational structure is typical of benzene and is referred to as the benzene absorption band (Fig. 12, *1*).

The "forbidden" band at $\lambda_{max} \approx 256$ nm is attributed to the presence of the antisymmetric vibrations in benzene which violate the symmetry conditions, and to the fact that the electronic motion in the molecule interacts with the electronic vibrations. The vibrational structure of the benzene absorption band is distinguished by the spacing of 923 cm^{-1} between individual peaks (Fig. 12, *1*). This value corresponds to the full-symmetry stretching vibration in the first excited electronic state of benzene (Fig. 12, *2*). The

spectra of benzene vapour exhibit the "hyperfine" structure (the "spikes") attributed to the rotational transitions. This structure appears owing to the fact that each vibrational level has a system of rotational sublevels. The band with fine vibrational-rotational structure at 230-270 nm makes the important difference between the spectra of benzene (alkyl benzenes) and those of the conjugated triene systems of the type



$\lambda_{max} = 303; \quad \varepsilon_{max} = 15000$

The alkyl substituents and halogens (Table 4) produce a slight bathochromic shift and an increase in the intensities of the bands at 200 and 256 nm; significantly, the vibrational structure of the spectra is retained. The capacity of atoms with unshared electron pairs for the p—π conjugation is determined by the position of the element in the periodis system, and the substituents in benzene derivatives form the corresponding series arranging the members by the respective bathochromic effect on the absorption bands (Table 4).

TABLE 4
THE EFFECT OF SUBSTITUENTS ON THE ABSORPTION BANDS OF MONOSUBSTITUTED BENZENE DERIVATIVES C_6H_5—R IN ALCOHOL

R	Band at 200 nm		Band at 256 nm		R	Band at 200 nm		Band at 256 nm	
	λ (nm)	ε	λ (nm)	ε		λ (nm)	ε	λ (nm)	ε
—	203	7400	256	220	OH	211	6 200	270	1450
CH_3	206	7000	261	225	SH	236	8 000	271	630
F	204	8000	248	500	NH_2	230	8 600	280	1430
Cl	210	7400	264	190	$H_2C=CH$	244	12 000	282	750
Br	210	7900	261	192	NO_2	259	8 000	—	—

Assuming that the shift of the long-wavelength band is a criterion of the p—π conjugation, we can see from the data of Table 4 that nitrogen is the most effective substituent in this respect as it produces a shift comparable to that of the double bond. The groups OH, OR and SH have lower but significant enough effect. The spectrum of nitrobenzene has the largest shift among other monosubstituted benzene derivatives (λ_{max} = 259 nm, $\varepsilon \approx 8000$). The spectrum for aqueous solution (λ_{max} = 266 nm) has a considerable bathochromic shift of 27 nm compared to that for the vapour (λ_{max} = = 239 nm) indicating a sharp increase in the dipole moment of the excited molecule (μ_g = 4.0 Debyes, μ_e = 10 Debyes). As mentioned above, this is a typical intramolecular charge-transfer band distinguished by a strong solvatochromic effect.

When the unshared electrons are blocked, for instance in the case of salt formation at the amino group ($C_6H_5\overset{+}{N}H_3\bar{C}l$), and no longer conjugated to the ring (there is only the induction effect) the absorption spectrum of the compound is close fo that of toluene C_6H_5—CH_3. Thus, the electron absorption spectra practically show no evidence of the induction effect tor $\pi \rightarrow \pi^*$ transitions.

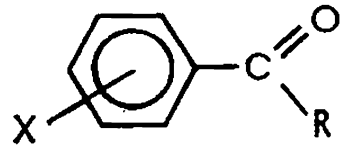
TABLE 5

THE SUBSTITUENT INCREMENTS

X	Alkyl	OH, O—R	O⁻	Cl	Br	NH_2	$NHCOCH_3$	$N(CH_3)_2$
Ortho	3	7	11	0	2	11	20	20
Meta	3	7	20	0	2	11	20	20
Para	10	25	78	10	15	58	45	85

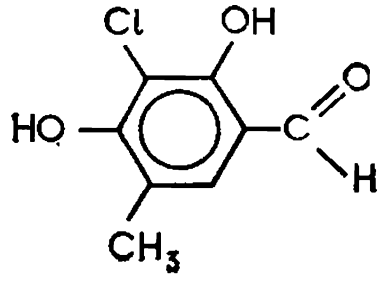
For the acceptor group C=O, there has been empirically derived a diagram for predicting the position of the charge-

transfer band according to the nature and position of the substituent, X. The wavelength is found by adding the increments for the substituent X (Table 5) to the wavelength λ_0 for the substituent R:



For R = alkyl, $\lambda_0 = 246$ nm; for OH and O, $\lambda_0 = 230$ nm; and for H, $\lambda_0 = 250$ nm.

For instance, for the compound



we obtain $\lambda_{pred} = (250 + 7 + 3 + 25)$ nm $= 285$ nm, $\lambda_{exp} = 287$ nm.

The Conjugation Effects in Electron Spectra

The interaction of electrons of a few multiple bonds giving rise to a single, delocalized electron cloud around all the atoms of the bond system, is known as the π—π conjugation. This conjugation is evidenced by typical changes in the electron absorption spectrum. If a molecule contains two unsaturated groups separated by carbon atoms, the absorption spectrum of this molecule is almost fully identical to the spectrum of the equimolecular mixture containing one of the unsaturated groups (Fig. 13). For the molecules of the A—$(CH_2)_n$—B type where A and B are the groups

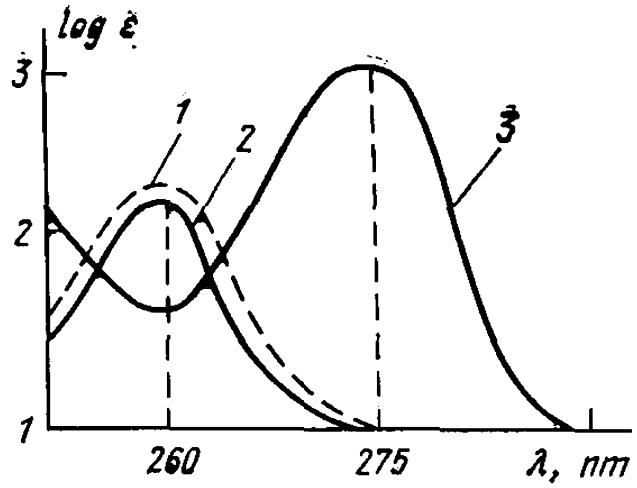


Fig. 13.
Conjugation effect on electron spectra: *1*—$C_6H_5(CH_2)_nCOOH$ ($n = 1, 2, 3$); *2*—$C_6H_5CH_2CH_3$ and CH_3COOH (1 : 1); *3*—C_6H_5COOH.

C_6H_5, CO, COOH, $CH{=}CH_2$, the absorption spectrum differs considerably from the spectrum of the mixture unless there are intermediate CH_2 groups between the groups A and B, that is, if A and B are conjugated (Fig. 13). When two (or more) unsaturated groups are conjugated the absorption bands are considerably shifted to longer wavelengths compared with the unconjugated chromophorms, and their intensities are increased. Let us consider the following typical illustrations.

Butadiene. Diolefins with two double bonds separated by methylene groups exhibit the same bands in the far ultraviolet region as monoolefins (Fig. 14 and p. 25). In butadiene the interaction between π levels of two ethylene groups

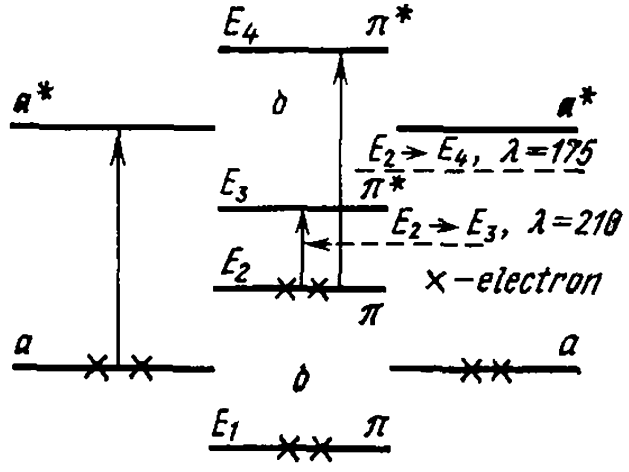


Fig. 14.
Energy levels of butadiene.

gives rise to the splitting of these levels. The result is the decrease in the energy difference between the upper occupied level E_2 and the lower free level E_3, and the spectrum contains a long-wavelength band for the $E_2 \rightarrow E_3$ transition at 210 nm in vapour and at 217 nm in hexane ($\varepsilon = 20\,000$).

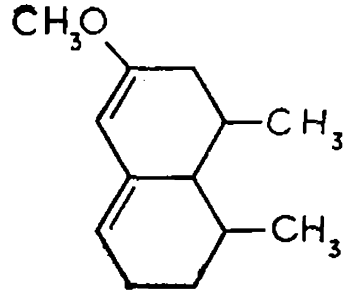
Woodward formulated a rule for predicting the positions of $\pi \rightarrow \pi^*$ bands of substituted dienes. The wavelength is calculated by adding the increments for substituents (Table 6) to the following baseline wavelengths: 217 nm for the *s-trans* position (heteroannular diene) or 214 nm for the cycle substituent; and 253 nm for the *s-cis* position (homoannular diene), as can be seen from Table 6.

TABLE 6

WOODWARD'S RULE FOR DIENES

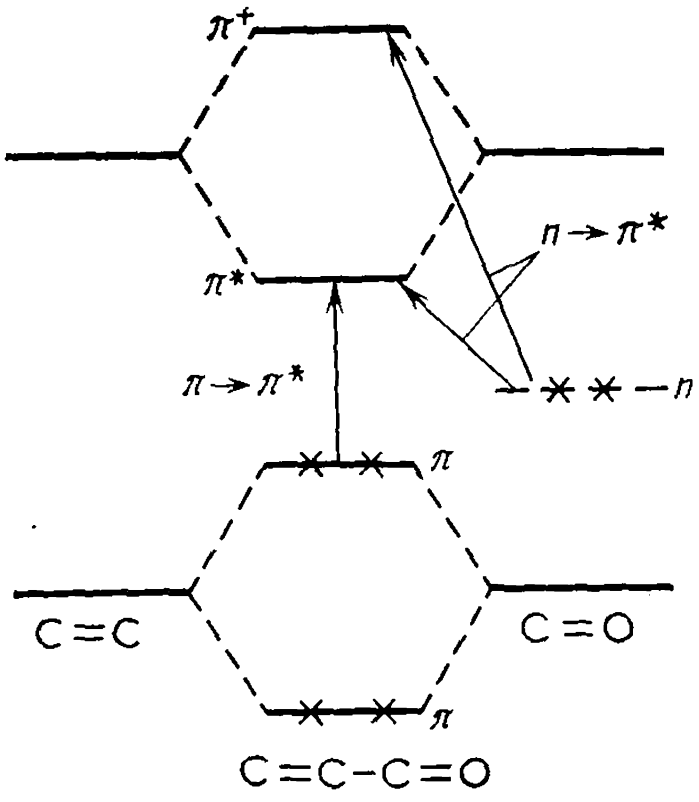
Substituent	Increment	Substituent	Increment
Alkyl, cycle group	5	Br	3-10
$O-C-CH_3$ (‖ O)	0	Double bond increasing the conjugation chain	30
O-alkyl, Cl	5	Exocyclic double bond	5

For instance, the compound



has the *s-trans*-diene system (in cycles), three cycle groups, a substituent OCH_3 and one exocyclic double bond. Accord-

Fig. 15.
The levels of conjugated carbonyl (actually, the levels C=C are higher than the levels C=O).



ing to Woodward, we find λ_{pred} = (214 + (3 × 5) + 5 + + 5) nm = 239 nm (λ_{exp} = 240 nm). The agreement with experimental results is good, the typical deviation being not more than 3 nm.

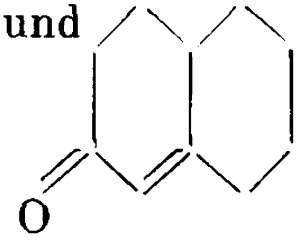
Unsaturated Carbonyl Compounds of the C=C—C=O Type. The spectroscopic properties of the α and β unsaturated carbonyl compounds are largely similar to those of dienes. Conjugation of the carbonyl group and the vinyl group requires that we consider a system of four π electrons and four electron levels two of which are occupied in the ground state (Fig. 15); *n* and σ levels remain unchanged while the difference between the upper occupied and lower vacant π levels decreases. Therefore, the $n \rightarrow \pi^*$ and especially the $\pi \rightarrow \pi^*$ bands are shifted to longer wavelengths while the $n \rightarrow \sigma^*$ and $\sigma \rightarrow \sigma^*$ bands remain unchanged.

Thus, the spectra of α and β unsaturated aldehydes and ketones have a high-intensity $\pi \rightarrow \pi^*$ band at 220-260 nm ($\varepsilon \approx 10\,000$) and an $n \rightarrow \pi^*$ band at 320 nm ($\varepsilon \approx 100$) (compare to: 163 nm for the $\pi \rightarrow \pi^*$ band of ethylene and

about 280 nm for the $n \rightarrow \pi^*$ band of saturated carbonyl compounds). The long-wavelength $\pi \rightarrow \pi^*$ band corresponds to a charge-transfer transition. The electron is transferred from the π orbital of the C=C bond to the excited π^* orbital of the C=O bond ($\rangle C{=}C{-}C{=}O \xrightarrow{h\nu} \rangle \overset{+}{C}{-}C{=}C{-}\bar{O}$).

Such a sharp change in the dipole moment accounts for the high sensitivity of these compounds (in contrast to dienes) to the solvent type; also, increasing polarity of the solvent (from hexane to alcohol) results in a hypsochromic shift of the $n \rightarrow \pi^*$ band and the bathochromic shift of the $\pi \rightarrow \pi^*$ band; hence, the spacing between them decreases.

For the α and β unsaturated carbonyl compounds, as for the dienes, there has been formulated a rule for predicting the position of the absorption band peak for a substituted compound. The wavelength $\lambda_0 = 215$ nm is taken as the baseline value (in ethanol). Then the following increments are added: +10 for alkyl (α position); +12 for alkyl (β position); +18 for alkyl (γ and δ positions); +35 for OH (α position); +30 for OH (β position); +5 for exocyclic double bond; and +30 for the double bond increasing the conjugation chain. For instance, for the compound



we obtain $\lambda_{pred} = (215 + 2 \cdot 12)$ nm = 239 nm (β, β-substituents) while $\lambda_{exp} = 241$ nm. However, it should be again emphasized that the band peak is rather sensitive to the nature of the solvent so that the following corrections for the solvents should be used (for the ethanol results): +1 for chloroform; +5 for dioxane; +7 for ether; +11 for hexane; and −8 for water (note the minus sign!).

Polyenes. Especially pronounced conjugation effects can be found in the spectra of polyenes. An increase in the length

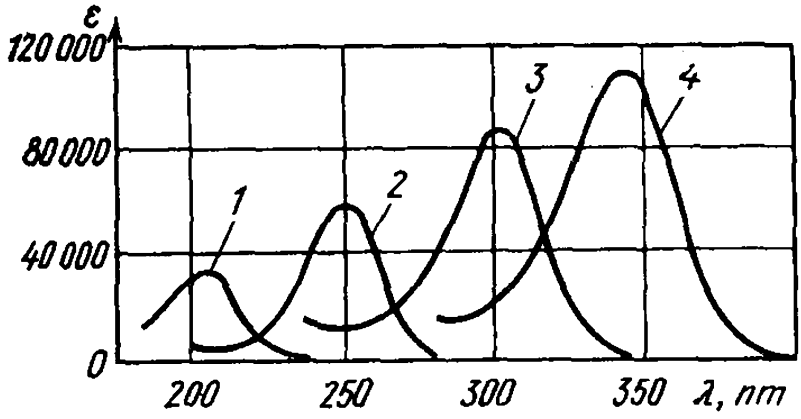


Fig. 16.
The shift and increase in the intensity of the long-wavelength band with an increase in the chain length of the conjugated bonds in the compounds of the type $CH_3—(CH=CH)_n—COOH$: *1*—$n = 1$, *2*—$n = 2$, *3*—$n = 3$, *4*—$n = 4$.

of the polyene chain (the conjugation chain) produces an increase in the peak wavelengths and the intensities of the absorption bands (Fig. 16). The absorption bands of the long polyene chains are shifted down to the visible range, that is, the compounds are coloured. The spectra of most polyenes exhibit a vibrational structure of the main absorption band. Replacement of the C=C group in polyene with the C≡C group practically does not change the band position but decreases the intensity. Compared to the linear dienes, cyclic dienes exhibit the absorption bands at longer wavelengths with reduced intensities.

Spatial Effects in Electron Spectra

As follows from the above discussion, the alkyl substituents in molecules have only a slight effect on the electron spectra. Noticeable effects occur only when the substituent significantly changes the length of the conjugation chain. This fact can be illustrated by the effect of the *ortho* alkyl substituents on the absorption spectrum of diphenyl.

The conjugation energy E is known to be related to the rotation angle θ by the following equation:

$$E = E_{max} \cos^2 \theta \qquad (12)$$

When the rotation angle is not more than 30° the variation of the conjugation energy is small; it decreases mostly with the rotation angle varying from 30° to 60° (see Fig. 17). If the rotation angle is close to 90°, conjugation is lacking owing to $E \approx 0$. For (unsubstituted) diphenyl $\theta \approx 45°$, $\lambda_{max} = 248$ nm and $\varepsilon_{max} = 19\,000$. The intensity is so high because the $\pi \rightarrow \pi^*$ transition is permitted owing to violation of the benzene symmetry. If a bulky substituent (for instance, CH_3) is inserted at the *ortho* position, the coplanarity of the two benzene rings is violated to a certain extent owing to overlapping of H and CH_3, and we have $\lambda = 236$ nm and $\varepsilon = 10\,000$. When two methyl groups are inserted at the *ortho* positions, there appears a new absorption band with $\lambda = 262$ nm and $\varepsilon = 800$, that is, the resulting spectrum is close to that of toluene ($\lambda = 262$ nm, $\varepsilon = 300$). This suggests that for conjugation violations the extinction

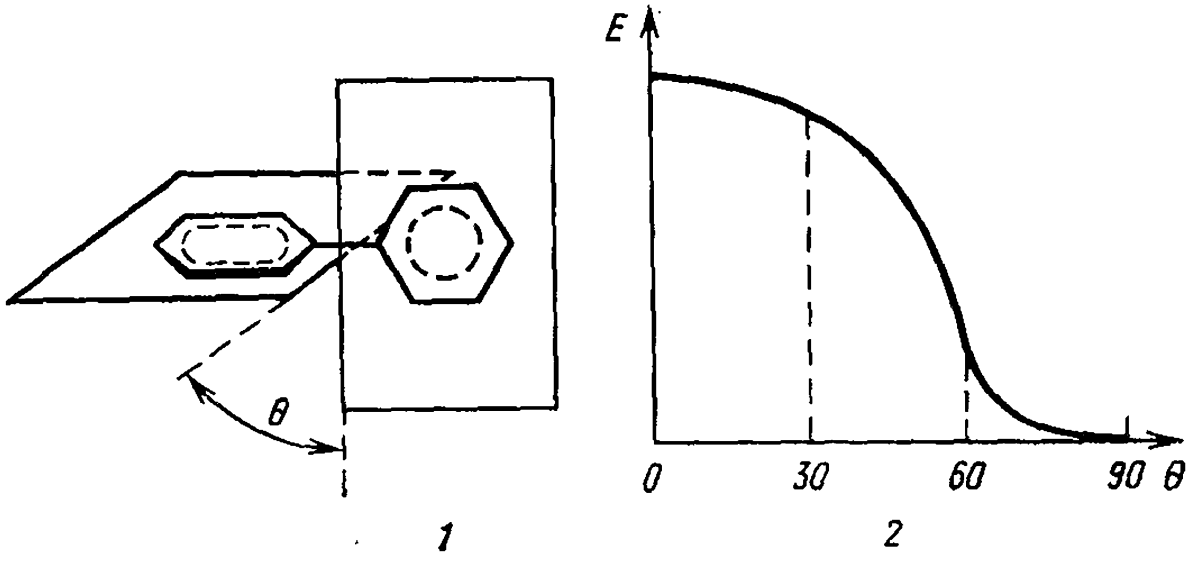


Fig. 17.
The arrangement of two benzene rings in a diphenyl molecule (1); the conjugation energy E as a function of the rotation angle θ (2).

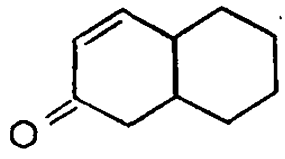
coefficient ε is a more informative parameter than the wavelength λ, and determines the degree of forbiddenness of the transition.

PROBLEMS IN ELECTRONIC SPECTROSCOPY

The problems in this chapter deal with the electronic absorption spectroscopy and the potentialities of this technique.

Problem 1. Calculate the wavelength λ_{max} of the electronic absorption spectra of the following carbonyl compounds in ethanol:

1.



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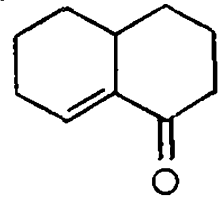
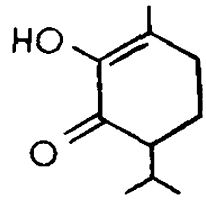
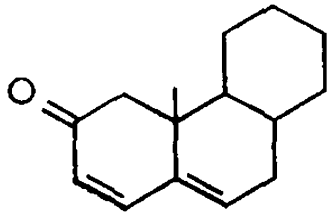


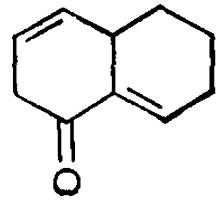
3.



4.



5.



Answer. The peak wavelength can be found from Woodward's rule using the peak wavelength of the basic system of these compounds (λ_0 = 215 nm) and adding to it the increments for the relevant substituents (see above p. 38).

1. 215 nm (α, β unsaturated ketone) + 12 nm (β substituent) = 227 nm. Experiment—230 nm.

2. 215 nm (α, β unsaturated ketone) + 12 nm (β substituent) + 10 nm (α substituent) + 5 nm (exocyclic double

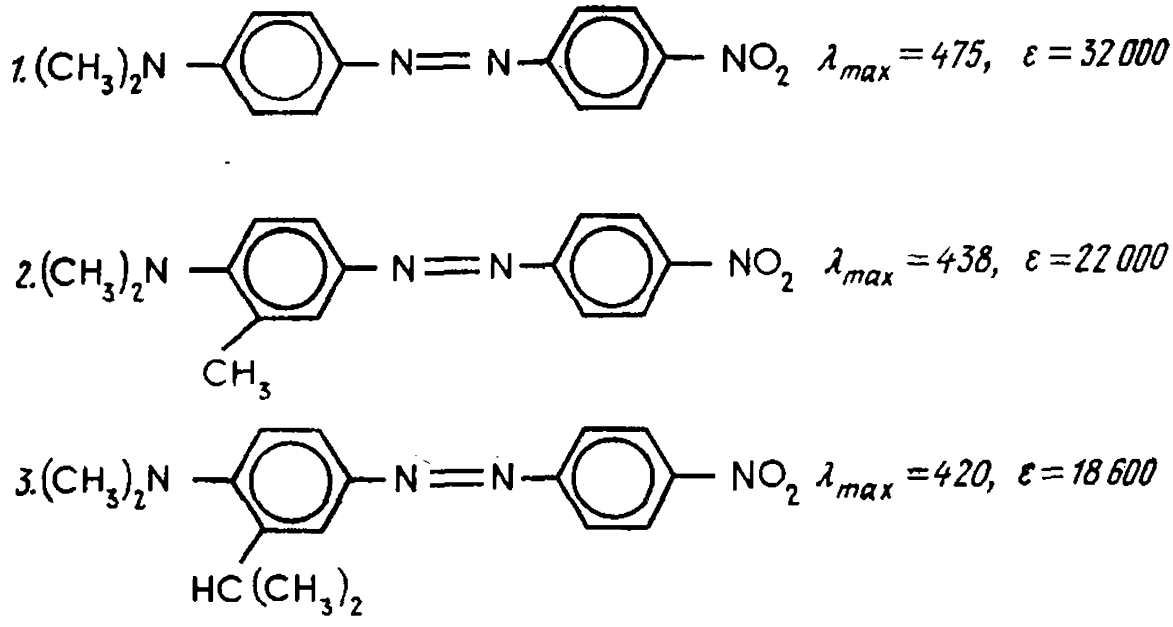
bond relative to the cyclohexane ring) = 242 nm. Experiment—243 nm.

3. 215 nm (α, β unsaturated ketone) + 12 nm·2 (two β substituents) + 35 nm (α-OH) = 274 nm. Experiment—270 nm.

4. 215 nm (α, β unsaturated ketone) + 30 nm (conjugated double bond) + 18 nm·2 (γ, δ ring groups) + 5 nm (exocyclic double bond) = 286 nm. Experiment—290 nm.

5. 215 nm (α, β unsaturated ketone) + 10 nm (α substituent) + 12 nm (β substituent) + 5 nm (exocyclic double bond) = 242 nm. Experiment—241 nm.

Problem 2. Explain the changes in the electron spectra of compounds (2) and (3) compared to compound (1) (in alcohol):


1. $(CH_3)_2N$ — N=N — NO_2 $\lambda_{max}=475$, $\varepsilon=32000$
2. $(CH_3)_2N$ — N=N — NO_2 $\lambda_{max}=438$, $\varepsilon=22000$
CH_3
3. $(CH_3)_2N$ — N=N — NO_2 $\lambda_{max}=420$, $\varepsilon=18600$
$HC(CH_3)_2$

Answer. In compound (1) the unshared electron pair of the nitrogen atom in the dimethyl amino group is conjugated with the benzene ring (p—π conjugation) while in compound (2) this conjugation cannot be complete owing to the methyl group at the *ortho* position.

When methyl at the *ortho* position is replaced by a more bulky group, namely, isopropyl, the peak wavelength is shifted still further (owing to full violation of conjugation)

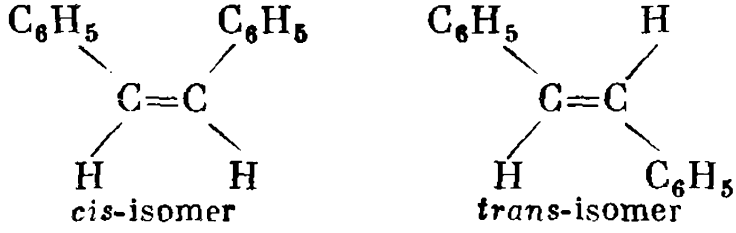
to shorter wavelengths (λ = 420 nm), with an accompanying drop of the band intensity (ε = 18 600).

Problem 3. A compound of the type of stilbene, cinnamic acid and azobenzene may exhibit different absorption properties under certain conditions, e.g.:

1. $C_6H_5HC{=}CHC_6H_5$—λ = 280 nm, ε = 13 500; or λ = 295 nm, ε = 27 000.
2. $C_6H_5HC{=}CHCOOH$—λ = 264 nm, ε = 9 500; or λ = 273 nm, ε = 20 000.
3. $C_6H_5N{=}NC_6H_5$—λ = 324 nm, ε = 15 000; or λ = 319 nm, ε = 20 000.

Explain these differences.

Answer. The above compounds have two isomeric forms—the *cis*- and *trans*-forms:



Since the geometrical isomers have different arrangements of the groups with respect to certain planes they should have different absorption spectra. This is illustrated by the absorption spectra of *trans*- and *cis*-stilbene in Fig. 18. It can be assumed that the absorption bands of the *trans*-

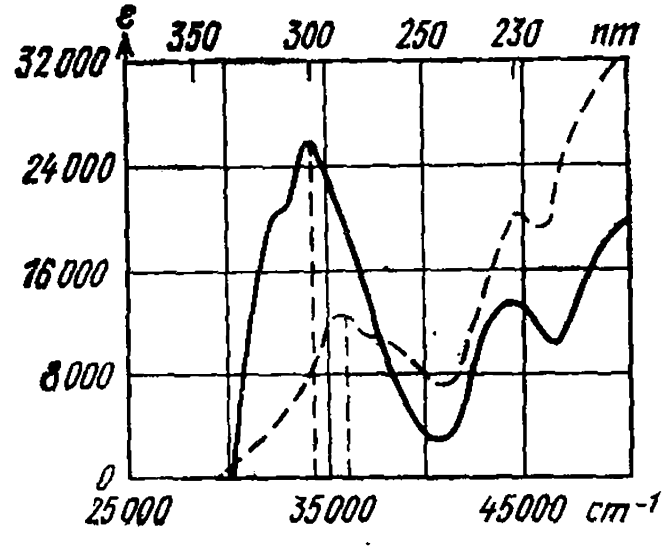
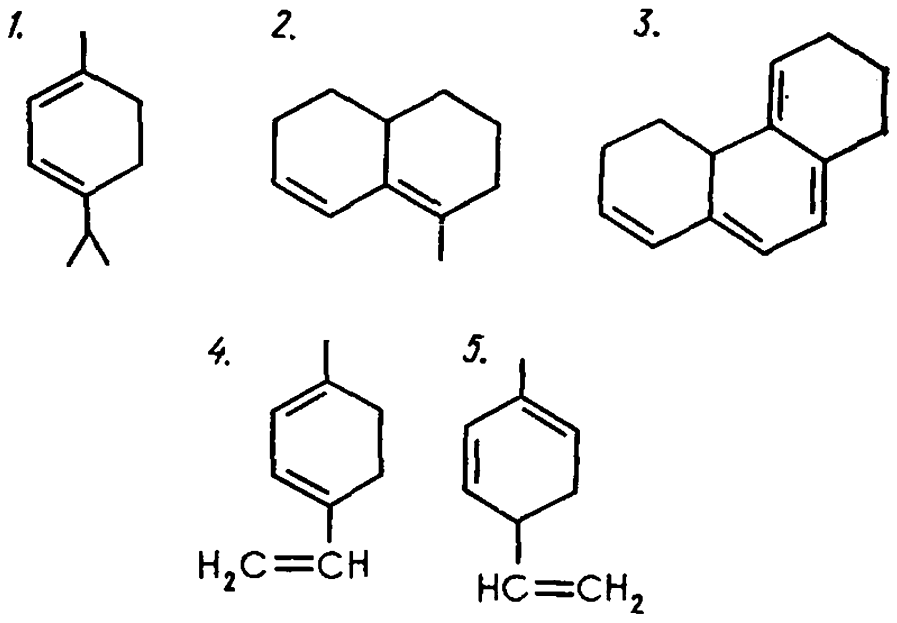


Fig. 18.
The absorption bands of *cis*-stilbene (dashed line) and *trans*-stilbene (solid line).

isomers at the long wavelengths always have higher intensities than the bands of the *cis*-isomers. Hence, for the above compounds the first band is the absorption band of the *cis*-form and the second one is produced by absorption of the *trans*-form.

Problem 4. Calculate the peak wavelengths of the electronic absorption bands for the following diene hydrocarbons (in alcohol):



Answer. Woodward's rule yields the following results for dienes:

1. 253 nm (homoannular diene) + 4 × 5 nm (two substituents and two cycle groups) = 273 nm. Experiment—272 nm.

2. 214 nm (heteroannular diene) + 4 × 5 nm + 5 nm (exocyclic double bond) = 239 nm. Experiment —238 nm.

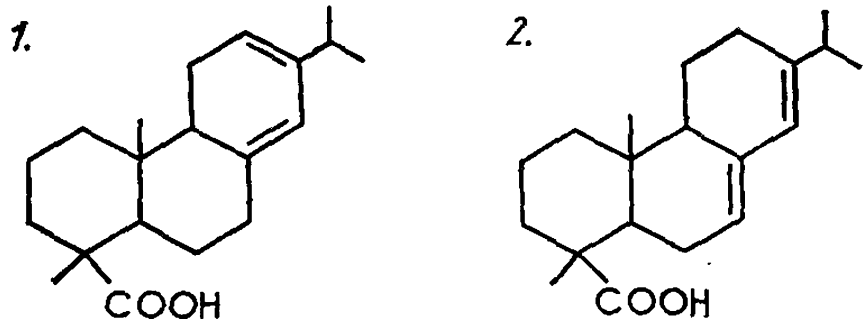
3. 253 nm (central homoannular diene) + 2 × 30 nm (two double bonds increasing the conjugation chain) + + 5 × 5 nm (substituents) + 3 × 5 nm (exocyclic double bonds) = 353 nm. Experiment—355 nm.

4. 253 nm (homoannular diene) + 4 × 5 nm (substituents) + 30 nm (double bond increasing the conjugation chain) = 303 nm. Experiment—298 nm.

5. 253 nm (homoannular diene) + 3 × 5 nm (substituents) = 268 nm. Experiment—269 nm.

Problem 5. The electronic spectral data can typically be used to make tentative assumptions rather than exact conclusions. However, in especially favourable cases electron spectra can yield almost exhaustive information on the structures of the compounds. This problem (and problem 6) illustrates this statement.

Two steroid dienes, namely the abietic and levopimaric acids, are isomers, they have the absorption bands at 241 nm (ε = 26 000) and 273 nm (ε = 6300):



Identify the structures of the acids, proceeding from the spectroscopic data.

Answer. Woodward's rule for dienes yields:

1. λ_{pred} = 253 nm + 4 × 5 nm = 273 nm;
2. λ_{pred} = 217 nm + 4 × 5 nm + 5 nm (exocyclic double bond) = 242 nm.

Clearly, compound (1) is the levopimaric acid and compound (2) is the abietic acid. It should be noted that the *cis* dienes exhibit typically lower-intensity absorption (ε varies between 5000 and 15 000) than the *trans* dienes (ε varies between 12 000 and 28 000), and the peak wavelengths of their absorption bands are found at lower frequencies (longer wavelengths).

Problem 6. The absorption spectra have shown the structural differences between the optically active antibiotic mycomycin (1) and its isomer isomycomycin (2) whose com-

mon empirical formula is $C_{13}H_{10}O_2$:

1. λ_{max} = 256, 267 and 281 nm;
   $\varepsilon_{max} \cdot 10^{-3}$ = 35, 61 and 67.
2. λ_{max} = 246, 258, 267, 288, 306, 324 and 347 nm;
   $\varepsilon_{max} \cdot 10^{-3}$ = 24, 58, 110, 14, 27, 41 and 34.

Hydration has revealed eight multiple bonds in these compounds and a carboxylic and terminal acetylene groups (in mycomycin) have been found. Proceeding from these data make a tentative determination of their structures.

Analyze the spectra of mycomycine and the triacetylene system conjugated with diene (3):

3. $CH_3—CH=CH—C\equiv C—C\equiv C—C\equiv C—CH=CH—CH_3$:
λ_{max} = 245, 259, 269, 289, 306, 325 and 348 nm;
$\varepsilon_{max} \cdot 10^{-3}$ = 25, 43, 76, 11, 18, 26 and 20.

Derive the structural formulas of the isomers.

Answer. The following two structures can be suggested from the empirical formula and the fact that the compound has the carboxylic group and the terminal acetylene group:

1. $HC\equiv C—C\equiv C—CH=C=CH—CH=CH—CH=CH—CH_2—COOH$;
2. $H_3C—C\equiv C—C\equiv C—C\equiv C—CH=CH—CH=CH—CH_2—COOH$.

Other possible structures of the compounds have lower probabilities as they would not agree with the electronic absorption spectra. Thus, a longer-wavelength band of isomycomycin indicates a longer conjugation chain as compared with mycomycin, and its position suggests the existence of five conjugated bonds (p. 39).

A comparison of the spectrum of mycomycin with that of the model compound (3) supports the above conclusions. The absorption bands of compound (3) are identical to those of isomycomycin suggesting that the latter contains a triyne fragment conjugated with diene, and that mycomycin has

the structure of the optically active cumulendiene diyne (1).

To compare the spectra of compounds being analyzed with those of the model compounds (whose structures are known) is the conventional (and often the only available) technique for structure determinations. The same technique is used for identifying unknown compounds.

Problem 7. The spectrum of 1,1-diphenylethylene (1) in cyclohexane differs considerably from that of anthracene (2). For compound (1) $\lambda_{max} = 250$ nm ($\varepsilon_{max} = 11\,000$) while compound (2) has two bands, $\lambda_1 = 252$ nm ($\varepsilon_1 = 200\,000$) and $\lambda_2 = 375$ nm ($\varepsilon_2 = 8000$). In concentrated sulphuric acid these compounds have very similar spectra:

1. $\lambda_1 = 315$ nm ($\varepsilon = 8000$), $\lambda_2 = 430$ nm ($\varepsilon = 30\,000$);
2. $\lambda_1 = 315$ nm ($\varepsilon = 12\,000$), $\lambda_2 = 425$ nm ($\varepsilon = 31\,000$).

In dilute acidic solutions these compounds have the same spectra as in cyclohexane.

What transformations occur in compounds (1) and (2)?

Answer. As the absorption spectra of compounds (1) and (2) are similar in sulphuric acid, this fact indicates the similarity of their electronic structures. In this solution the compounds add a proton, giving rise to almost identical ions (see Fig. 19).

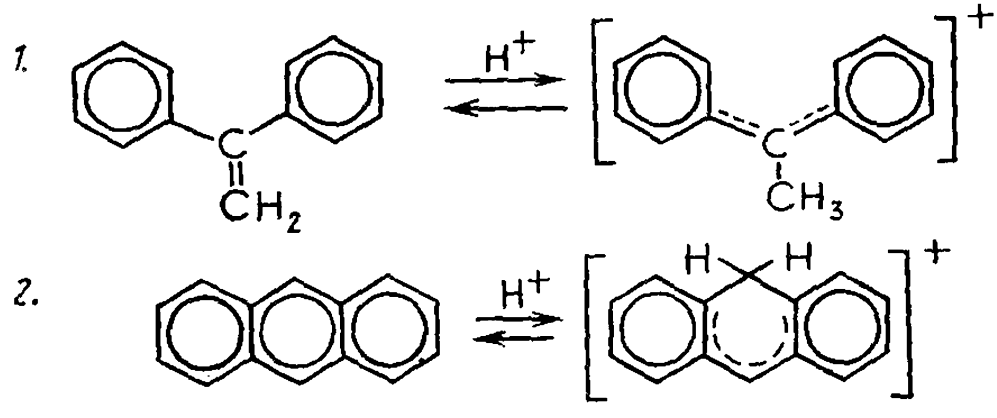
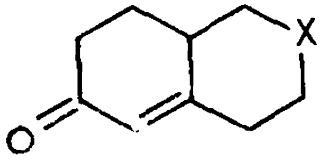


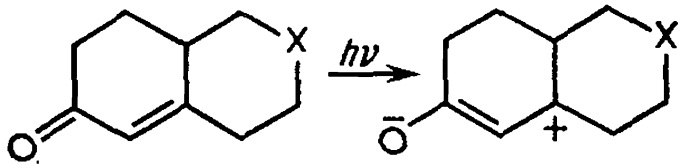
Fig. 19.
Formation of carbonium ions of 1,1-diphenylethylene and anthracene in sulphuric acid.

In dilute acidic solutions the equilibrium shifts toward starting compounds, that is, 1,1-diphenylethylene and anthracene, which have markedly different spectra.

Problem 8. Give the explanation of the fact that replacement of the group CH_2 by the group $>\overset{+}{N}(CH_3)_2\ \overset{-}{ClO_4}$ at the position X shifts the absorption band peak to a shorter wavelength in the ultraviolet range (from 238 nm to 229 nm):

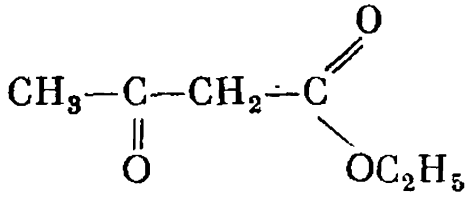


Answer. The absorption bands are due to the $\pi \rightarrow \pi^*$ transition in α, β unsaturated ketone, which can be approximately illustrated by the following scheme:



Separation of charges in the excited state is much greater than in the ground state. Insertion of the positive charge (the group $>\overset{+}{N}(CH_3)_2$) at the position X results in a higher energy of the excited state (a higher π^* level) so that the wavelength of the light triggering this transition is shifted to a shorter value (a higher quantum energy is needed).

Problem 9. The spectrum of acetoacetic ester (AAE)



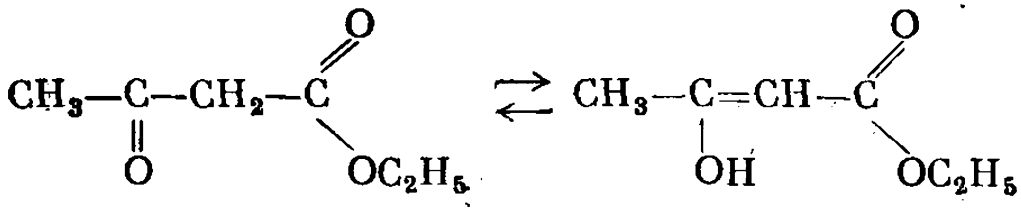
depends significantly on the nature of the solvent and on its concentration (Table 7). Explain this dependence.

TABLE 7

THE WAVELENGTHS AND INTENSITIES OF THE ABSORPTION SPECTRA OF AAE IN VARIOUS SOLVENTS

Solvent	λ_{max} (nm)	ε (log ε)	Solvent	λ_{max} (nm)	ε (log ε)
Hexane	244	8100 (3.91)	Alcohol	246	1900 (3.28)
Ether	244	5100 (3.71)	Water	255	120 (2.08)

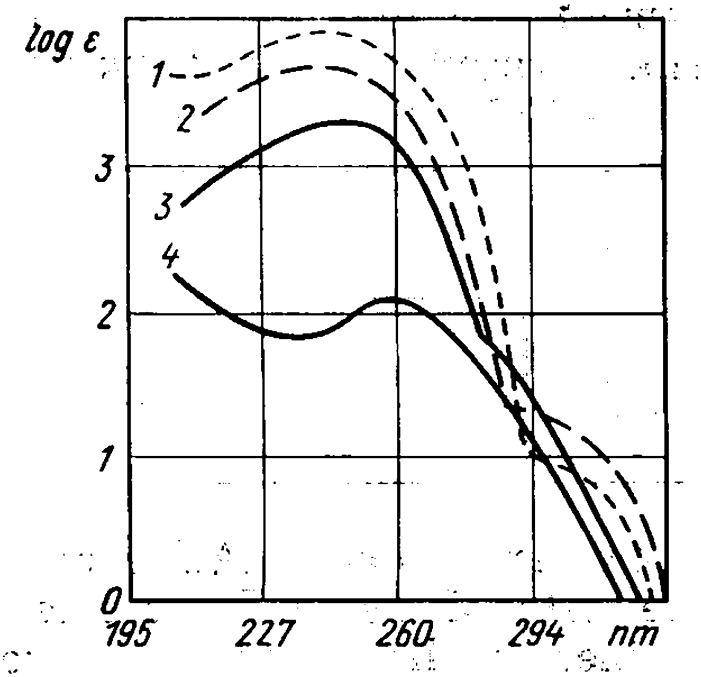
Answer. Though AAE should have low-intensity bands, the data of Table 7 indicate otherwise. This can be explained as follows. If carbonyl-containing compounds have at least one hydrogen atom at the α position, they can be enolized by transfer of the proton from carbon to oxygen:



These compound forms have different spectra since the starting compound (at the left) has the ketone form ($\varepsilon \approx 20$) and an isolated carbethoxy group producing the absorption band at 200 nm. The enol form (at the right) is an α, β unsaturated ester (conjugated system) and the hydroxyl group produces a bathochromic shift of the absorption band peak to 245 nm ($\varepsilon = 18\,000$). Fig. 20 presents the absorption curves of AAE in various solvents.

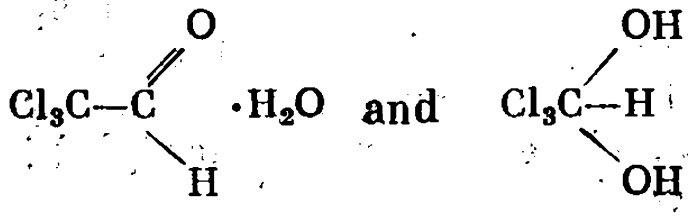
When the solvent is replaced by another one the equilibrium is shifted changing the percentage of the enol form responsible for high-intensity absorption. In water solution the enol form is practically nonexistent, the compound is in the ketone form which has a low-intensity absorption ($\varepsilon = 120$). Variation of the AAE concentration (in the same solvent) results in the processes typical of the equilibrium

Fig. 20.
The absorption band for acetoacetic ester in various solvents: *1*—hexane, *2*—ether, *3*—alcohol, *4*—water.



processes (the Beer-Lambert-Bouguer law is not satisfied in this case).

Problem 10. One of the earliest determinations of the structure of an organic compound from the absorption spectrum was that for chloral for which the following two isomeric structures were suggested:



Analyze the UV spectra of chloral in hexane (λ_{max} = = 290 nm, ε = 33) and water, and identify the structure (Fig. 21). Explain your answer.

Answer. The UV spectrum of chloral in hexane has one band at 290 nm with the extinction coefficient of about 33. This low-intensity band is typical of the carbonyl group suggesting the first structure. However, the IR spectrum of chloral in water does not show absorption at 290 nm, it has only the end of the far-ultraviolet (vacuum) absorption band. This indicates disappearance of the carbonyl group

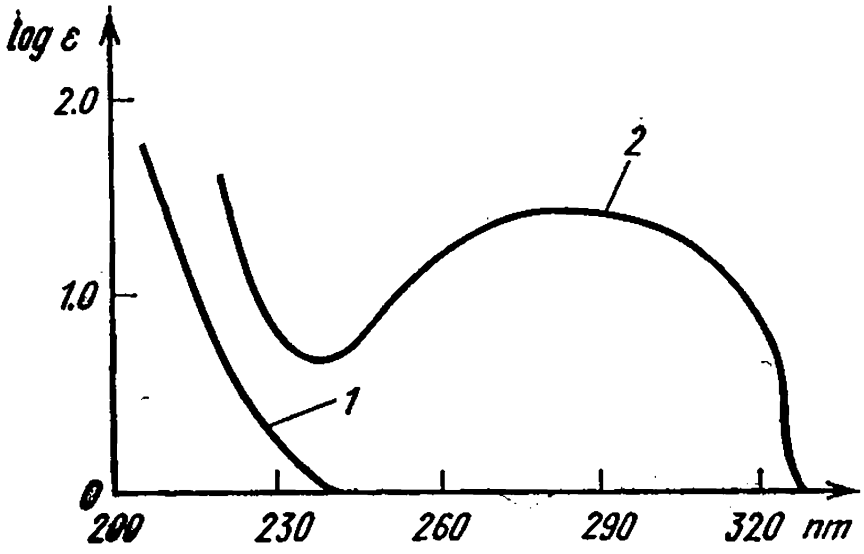


Fig. 21.
UV spectra of chloral in water (1) and hexane (2).

suggesting the structure of 1,1-dioxy-2,2,2-trichloroethane for chloral hydrate.

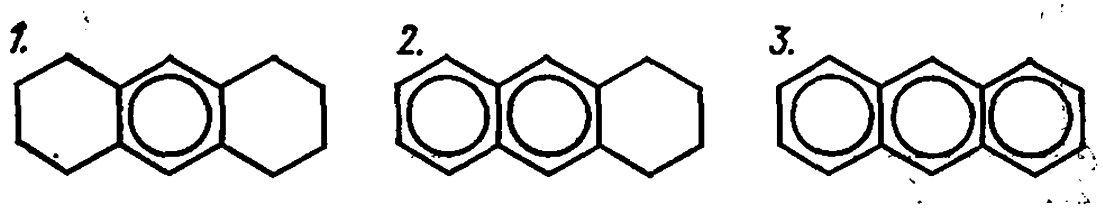
Problem 11. Explain the differences between the electron spectra of *p*-dialkylaminobenzoic acid in the following solvents:

1. Ethyl ether: $\lambda = 277$ nm, $\varepsilon = 20\,600$;
2. Ethanol: $\lambda = 288$ nm, $\varepsilon = 19\,000$;
3. Hydrochloric acid: $\lambda = 270$ nm, $\varepsilon = 970$.

Answer. The high intensities of the spectra in ethanol and ether indicate that this band is a typical $\pi \rightarrow \pi^*$ band while its bathochromic shift, when ether is replaced by ethanol, suggests that it has the intramolecular charge-transfer origin. The bathochromic effect here is due to the fact that the dipole moment of the molecule in the excited state is higher than the dipole moment of the ground state. The sharp difference of the spectrum for the solution in hydrochloric acid is caused by the violation of the $p \rightarrow \pi^*$ conjugation owing to the interaction between the unshared electron pair of

nitrogen and the proton (similar to problem 2 though the same effect of conjugation violation is caused there by steric factors).

Problem 12. Three linear tricyclic systems have the following formulas:



Their spectra shown in Fig. 22 have considerably different intensities and positions of the long-wavelength band with the fine vibrational structure. Dehydration should give rise to additional double bonds in the structure (1). Analyze the spectrum of the respective reaction product (Fig. 23), plot

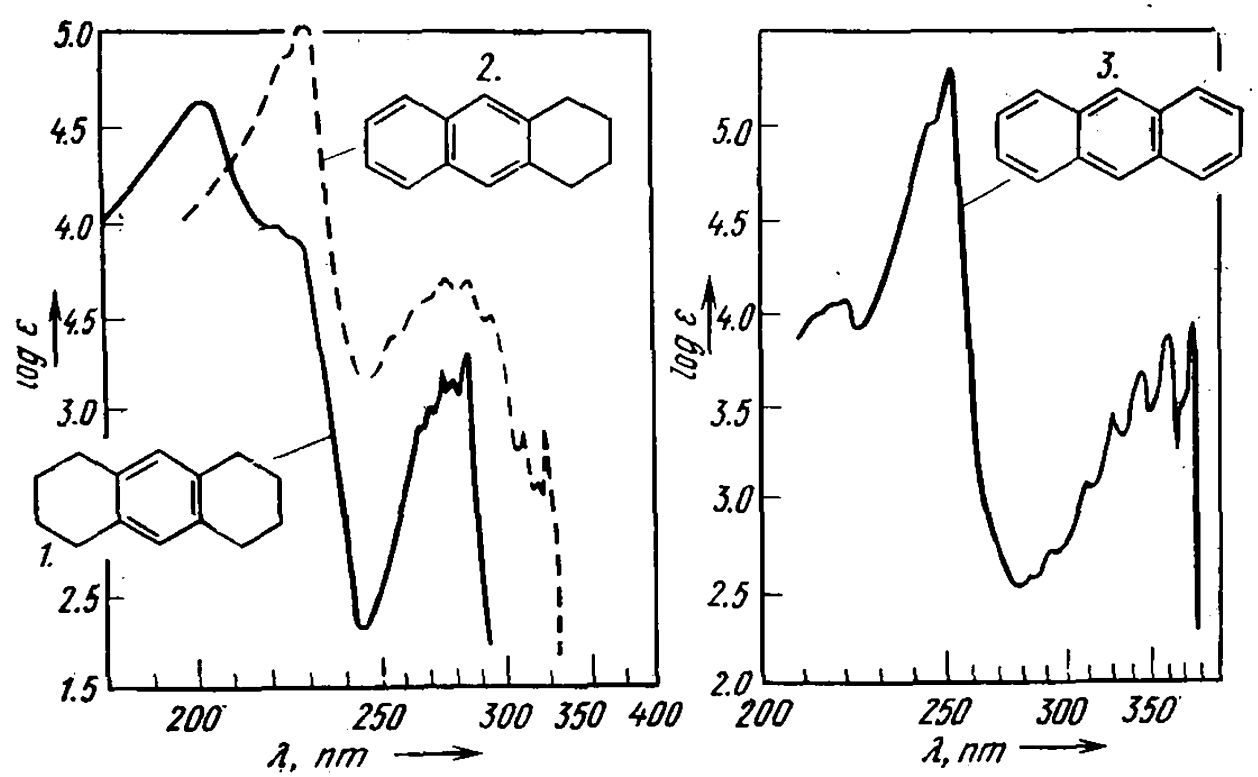
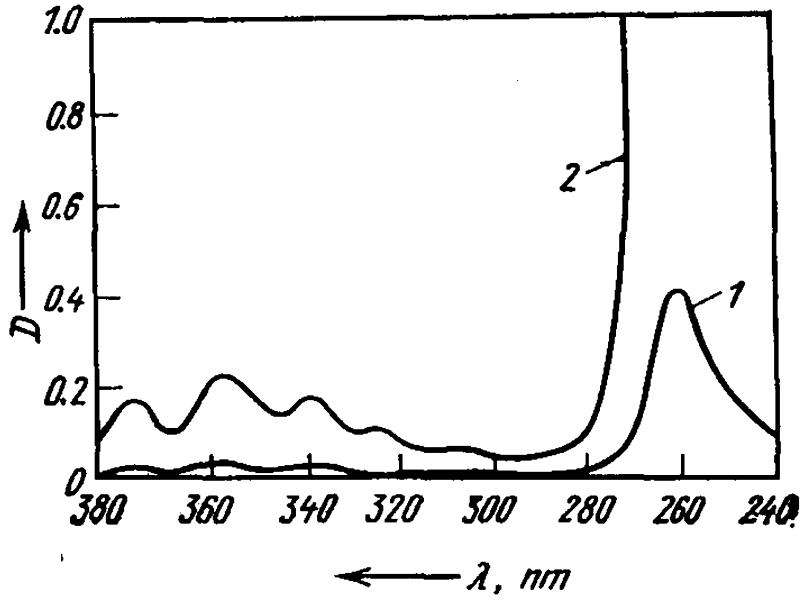
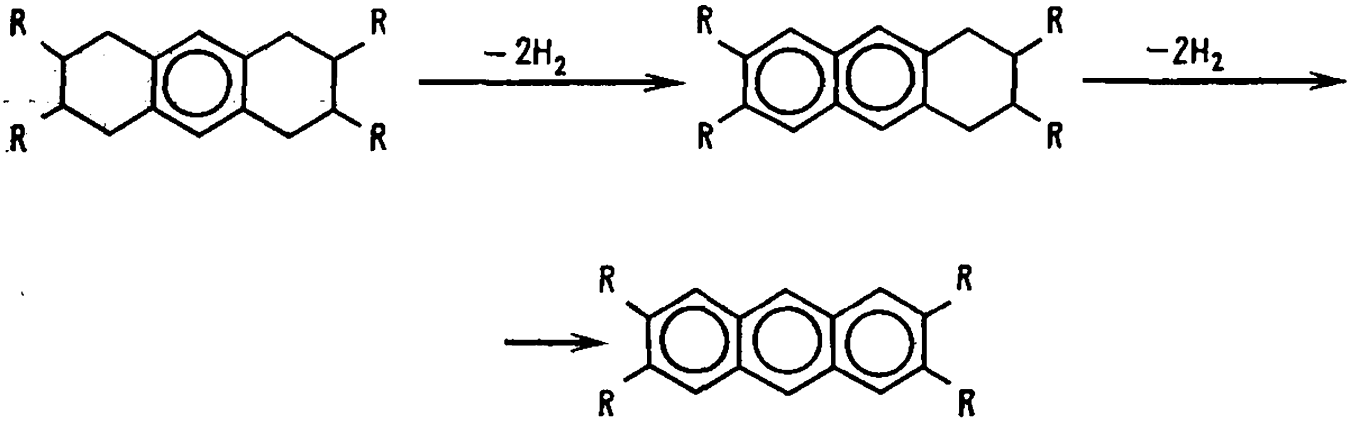


Fig. 22.
Electron spectra of tricyclic structures.

Fig. 23.
UV spectra of reaction products (see Problem 12).



it in the log ε vs. λ coordinates, and determine the extent of dehydration:



The conditions of spectra recording (Fig. 23): *1*—1.31 mg in 10 ml dioxane, 1: 99 dilution, $l = 1$ cm, $M = 410$; 2—dilution 1: 9, the remaining conditions are the same.

Answer. First, the molar concentration of the compound in both cases should be determined using the equation

$$c = \frac{m}{Mv}$$

Then the extinction coefficient ε should be found from eq. (10) and the characteristic points (maximums and mini-

mums) of the spectrum to plot log ε as a function of λ. Comparing the plot with the spectra of the above compounds demonstrates that the compound has the structure (3). Thus, dehydration is complete.

Problem 13. Assign two absorption bands of mesityl oxide (see Table 8) to a specific solvent (isooctane, methanol or water) and explain the differences in the spectra.

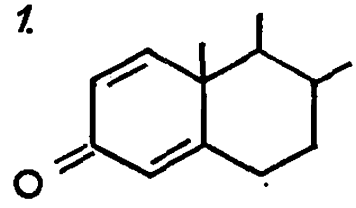
TABLE 8

Solvent	Band 1 λ_{max} (nm) (ε)	Band 2 λ_{max} (nm) (ε)
1	230 (12 000)	321 (38)
2	237 (11 000)	315 (57)
3	243 (10 000)	309 (100)

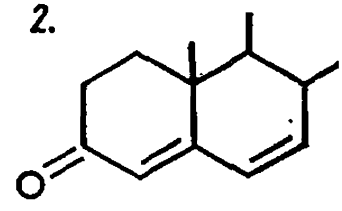
Answer. The band intensities suggest that the band at 310 nm is due to a $n \rightarrow \pi^*$ transition and the band at 230 nm is due to a $\pi \rightarrow \pi^*$ transition. As the polarity of the solvent increases the $n \rightarrow \pi^*$ transitions are shifted to shorter wavelengths so that we can identify the solvents: *1*—isooctane, *2*—methanol, and *3*—water. This is shown also by the bathochromic shift of the $\pi \rightarrow \pi^*$ transition in the 1 to 3 series of solvents.

Problem 14. Identify which one of the following two isomers has the electronic absorption band with $\lambda_{max} = 241$ nm and $\varepsilon_{max} = 18\,000$:

1.

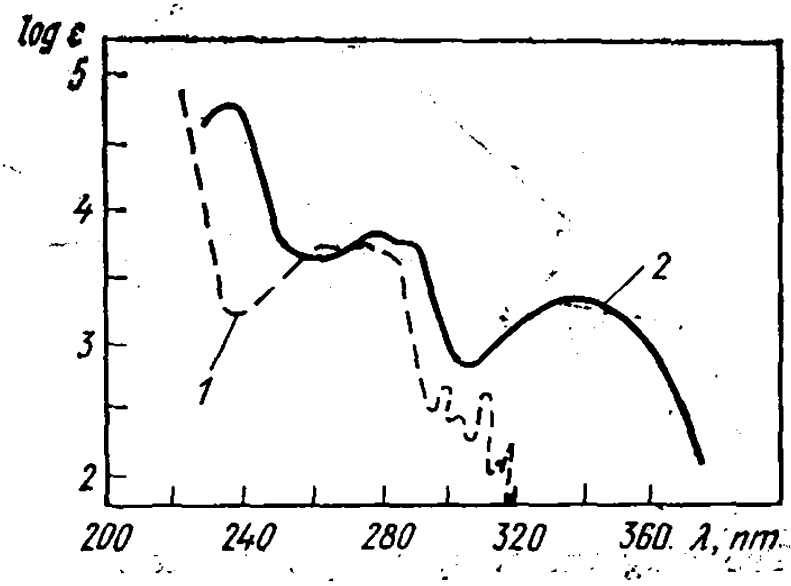


2.



Answer. For isomer *1* we find $\lambda = 215$ nm + 2·12 nm (two β substituents) = 239 nm; for isomer *2* $\lambda = 215$ nm +

Fig. 24. UV spectra of α-naphthylamine.



+ 12 nm (β substituent) + 30 nm (the double bond increasing the conjugation chain) + 18 nm (γ substituent) + 5 nm (exocyclic double bond) = 280 nm. Hence, the absorption spectrum has been measured for isomer *1*.

Problem 15. Fig. 24 presents the UV spectra of α-naphthylamine in alcohol solution and in acidic alcohol-water solution. Assign the spectra to the solvents.

Answer. The interaction between proton in the acidic medium and the unshared electron pair of nitrogen causes the amino group to lose conjugation, so that the spectrum of the compound should be close to that of naphthalene. Comparing the spectrum with that of the structure *2* in Fig. 22 we can see that the dashed spectral curve corresponds to the acidic alcohol-water solution, and the solid curve to the alcohol solution.

LABORATORY EXERCISES

The Fundamental Design of the Spectral Instrument

Various types of optical spectrophotometers are used for recording spectra in the infrared, visible, ultraviolet and vacuum ultraviolet ranges. An instrument of any type has

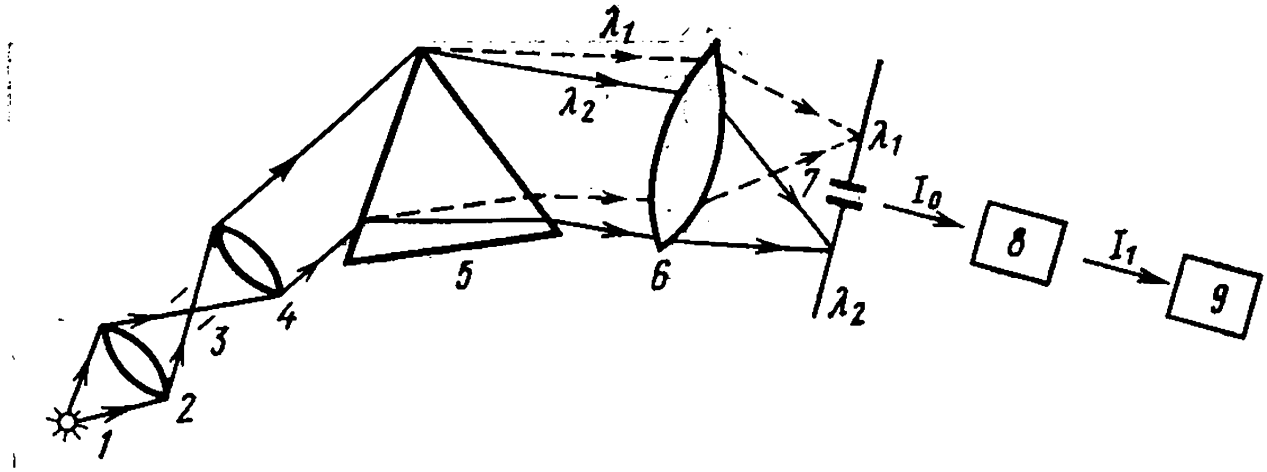


Fig. 25.
The diagram of spectrophotometer.

three principal components (Fig. 25): the source of electromagnetic radiation (*1*), the monochromator (*2-7*), and the detecting and recording unit (*9*). Fig. 25 presents a schematic diagram of the spectrophotometer. The radiation of a complex spectral composition from the source *1* is focussed by the lens *2* on the entrance slit *3*. The beam is collimated (made parallel) by the objective *4* and the collimated beam proceeds to the dispersing element *5* (a prism or a diffraction grating). The dispersing element forms the spectrum, in other words, it breaks down the beam into its spectral components, that is, spatially separates the rays with different wavelengths. The objective *6* makes up a system of monochromatic images of the entrance slit from the system of parallel beams of distinct wavelengths. The exit slit "cuts out" the required spectral interval. Rotating the dispersing element *5* we can scan the spectrum and focus on the exit slit the rays with chosen wavelength. The intensity I_0 of the light flux passing through a cell *8* containing the analyzed sample is reduced to I_1 owing to light absorption. The optical density of the material, $D = \log (I_1/I_0)$, is recorded by the system *9* (a photocell, a photomultiplier, etc.).

The Radiation Sources. The spectrophotometers recording the electronic spectra make use of the light sources of two

types—the hydrogen (deuterium) lamp with the 200-350 nm range, and the incandescent lamp with the range from 350 nm to longer wavelengths.

Monochromator. The monochromator is an essential part of any spectrophotometer. The basic element of the monochromator is the dispersing element which is a prism of fused or natural quartz for the ultraviolet spectra (glass is opaque for short-wave radiation). The basic parameters of the monochromator are the resolving power, the linear dispersion, and the transmission.

The linear dispersion is the ratio of the spectral interval to the respective linear interval in the plane of the spectral image:

$$D = \frac{\Delta l}{\Delta \lambda}, \quad \text{where} \quad \Delta\lambda = \lambda_1 - \lambda_2 \tag{13}$$

The larger the dispersion D the larger the spacing between the spectral lines. The parameter typically used in spectrophotometry is the inverse linear dispersion $d\lambda/dl$ (nm/mm) which gives the spectral interval in nanometers per 1 mm of the spectrum, thus characterizing the monochromaticity of the beam.

The dispersion D can be used to derive an important parameter of the monochromator, the spectral slit width S which equals the wavelength interval $\Delta\lambda$ cut out by the exit from the spectrum:

$$S = \frac{1}{D} \cdot h = \frac{\Delta\lambda}{\Delta l} \cdot h \tag{14}$$

The resolving power R gives the minimum distance between two spectral lines which can be resolved (that is, separate in the spectrum) by this monochromator. Fig. 26 illustrates resolution of two bands, and a lack of resolution. In other words, the instrument cannot resolve two monochromatic rays of the same intensity whose wavelengths differ by the spectral slit width. The resolving power depends

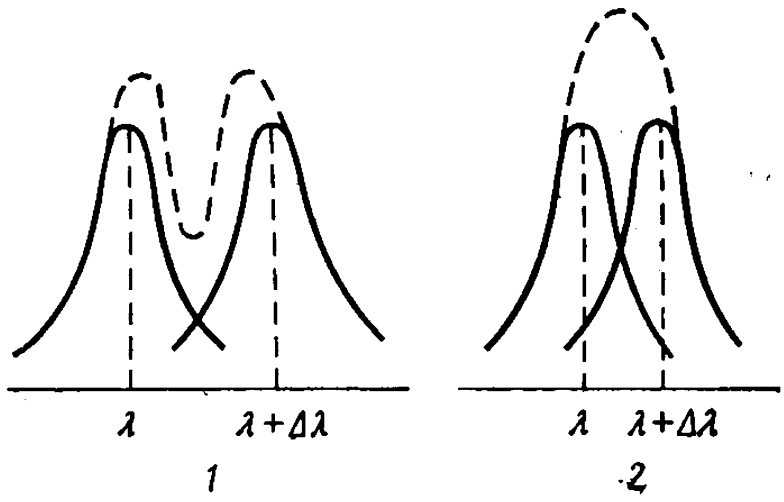


Fig. 26.
The spectra with resolved bands (1) and unresolved bands (2).

on the spectral region:

$$R = \frac{\lambda}{\Delta\lambda} \tag{15}$$

The transmission S_m of the monochromator characterizes the maximum light flux which can be passed through this instrument. Typically, the transmission is expressed in terms of the focal ratio of the monochromator:

$$S_m \approx (d_1/f_1)^2 \tag{16}$$

where d_1 and f_1 are the diameter and the focal distance of the objective *4*, respectively.

The Main Spectrophotometer Models Used in the USSR

Both nonrecording and automatically recording spectrophotometers are used in modern spectroscopy. The СФ-4А spectrophotometer is the one used most widely in the USSR. In this instrument the beam is divided in two and alternately measured after passing through the analyzed material and a reference (typically, a solvent). The optical densities for various wavelengths are determined and the spectral curves are plotted from these data. The instruments СФ-11, СФ-5, СФ-4 and СФ-16 have the same basic design as СФ-4А.

A widely used СФД-2 instrument differs from СФ-4А in that its dispersing element is a diffraction grating instead of a prism. In contrast to a prism, a grating has a constant dispersion over the entire spectral range. The instruments СФ-8 and СФ-20 are double-beam spectrophotometers with automatic recording of results; this eliminates the need for time- and labour-consuming point-by-point recording of spectra. The spectral instruments measure the optical density to the accuracy of 1%, and the wavelength to 1 nm.

Procedures for Recording Electron Absorption Spectra

The accuracy of measurements is a very important characteristic of the experiment. The inaccuracies caused by the errors of the operator (in preparing the initial solutions, filling the cells, etc.) and by the chemical reaction conditions (decomposition of reactants, intermolecular interactions, etc.) should be eliminated or minimized. However, some errors can be inherent in the operation of the instrument itself.

Instrument-related Deviations from the Beer-Lambert-Bouguer Law. The main causes of inaccuracies are a too large slit width and too short scanning time.

The spectral slit width S has a significant effect on the form of the absorption spectrum. Fig. 27 illustrates variation of the intensity with S; with increasing S the maximum intensity decreases and the band widens, that is, the spectrum is distorted. To eliminate distortion, the spectral slit width must be considerably smaller than the half-width $\Delta\nu_{1/2}$ of the band:

$$S \leqslant 0.2\Delta\nu_{1/2} \qquad (17)$$

For instance, the 1-mm slit of the spectrophotometer СФ-16 has the spectral width of 400 cm^{-1} for the 250-nm

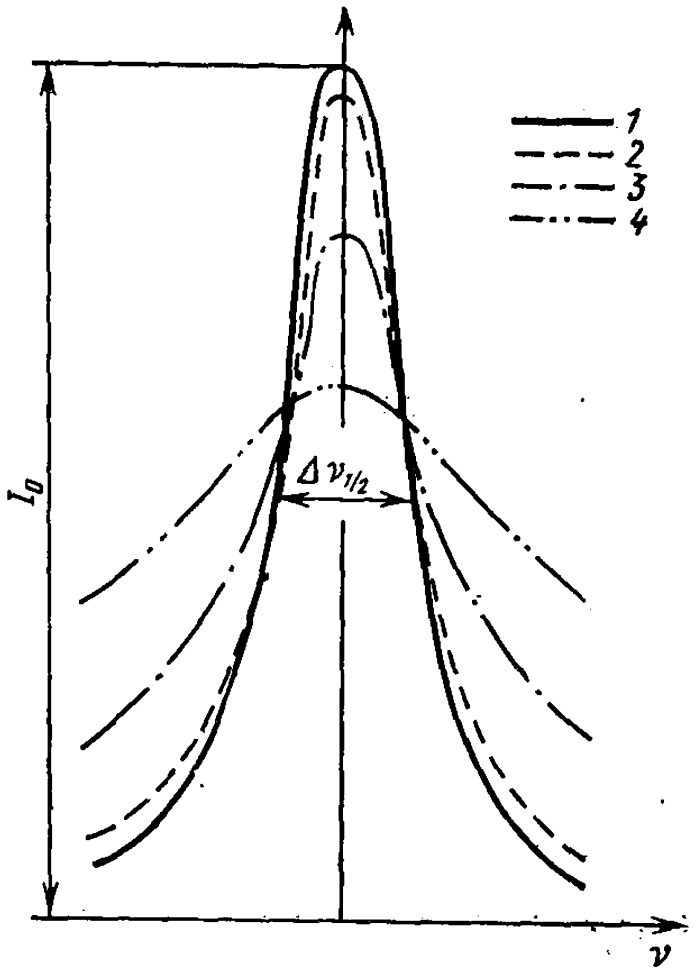


Fig. 27.
Variation of the band contour with the spectral width of the slit: $S/\Delta\nu_{1/2} = 0$ (1), 0.1 (2), 0.5 (3), 1.0 (4).

band. Thus, the condition (17) is satisfied for the nitrobenzene band at 260 nm (half-width of 5000 cm^{-1}) and is not satisfied for the benzene band at 250 nm (half-width of 300 cm^{-1}).

The speed v of scanning the spectrum is also an important factor determining the accuracy of spectra recording:

$$v = \frac{d\lambda}{dt} \quad \text{or} \quad v = \frac{d\nu}{dt} \tag{18}$$

Here the distortions are due to the fact that the recording system of any instrument possesses certain inertia (response time), and cannot instantaneously respond to a sharp variation of absorption. The spectra with narrow absorption bands should be recorded at the lowest scanning speed available. As the scanning speed increases (Fig. 28), the distortions become more pronounced affecting all the parameters of the band, that is, its intensity at the maximum, width, shape and

even the position. To eliminate these distortions the time of recording of a band must be larger by an order of magnitude than the response time τ of the recording system:

$$v \leqslant \frac{\Delta\nu_{1/2}}{10\tau} \tag{19}$$

Noise. Another factor affecting the accuracy of spectra recording is the noise which appears in the process of signal conversion, and is recorded by the instrument. The maximum signal-to-noise ratio providing for the best spectrophotometric accuracy is found in the optical density range from 0.3 to 0.8. By varying the thickness of the material being analyzed and the solution concentration we can bring the optical density to this range.

Solvents. The solvents used for spectroscopic applications must satisfy the following conditions (for the UV, IR, Raman and NMR spectroscopy): transparency in the analyzed

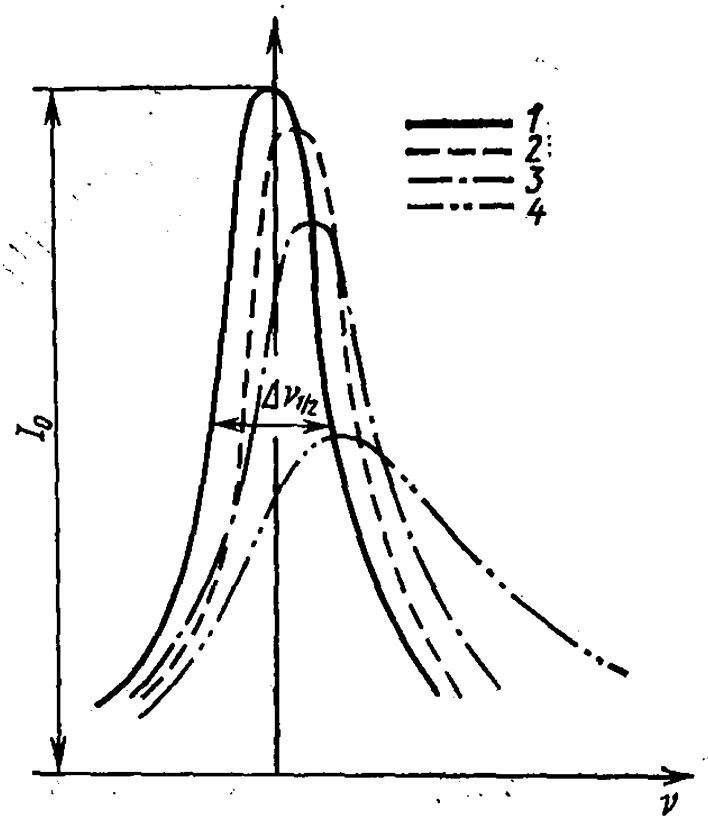


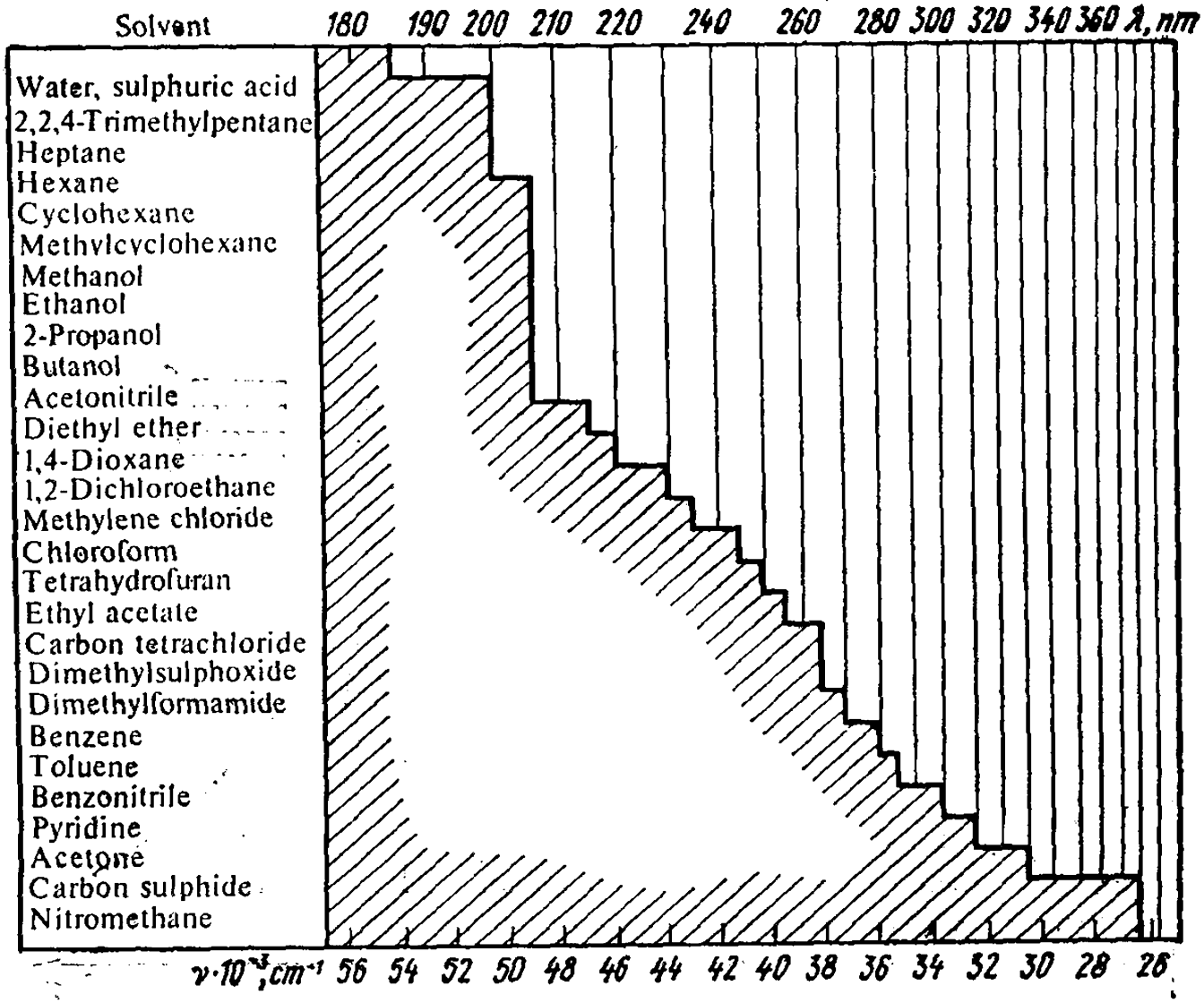
Fig. 28.
Variation of the position and contour of the band with scanning speed (*1*—the true band, *2*, *3*, *4*—distorted bands).

region, sufficient dissolving power, resistance to the analyzing radiation, lack of reactivity towards the analyzed compounds, and negligible intermolecular interactions with the dissolved compound. However, it is not infrequent that it is precisely the change of the absorption spectrum due to interaction with the solvent that yields valuable information on the analyzed compound.

Table 9 shows the transmission ranges of the solvents

TABLE 9

TRANSMISSION RANGES OF THE SPECTRALLY PURE SOLVENTS FOR 1-cm LAYER (accuracy ± 5 nm)



typically used in the IR spectroscopy. The most convenient solvents are the saturated hydrocarbons and fluorocarbons as they have negligible intermolecular interactions and lack the easily excitable optical π electrons. As the thickness of the layer is decreased the edge of the transmission region shifts markedly to shorter wavelengths. The solvents are, typically, purified before use.

Solution Concentrations. To provide for the optimum optical density (about 0.5) of the solution of the compound with the extinction coefficient about 10 000 the concentration must be 10^{-4} mole/l (about 10^{-2} g/l) for 1 cm thick layer. The solution volume for spectrum recording is typically not more than 10 cm^3, so that the weighed amount of the material must be about 0.1 mg. Thus, to increase the accuracy of dissolving, the solution should be prepared by consecutive dilutions.

Recording of the Absorption Spectra in Solid Samples. Spectrophotometry of solid samples encounters difficulties produced by losses of light on reflection and scattering at each surface. Therefore, a solid to be analyzed is pressed into a tablet with a transparent filler which does not absorb radiation in the analyzed range. A pellet of a pure filler is used as the reference. Sometimes the solid is prepared in the form of suspension in the mineral oil.

Cells. Typically, analysts use rectangular cells with the path length of about a few centimeters. However, when the bands have very high intensities, it is necessary to use very short path lengths (0.1-0.005 cm). Demountable cylindrical cells with inserts are used to this end. Thermostatted cell holders are needed for studying kinetic effects and equilibrium processes.

Reflection Measurements. Special attachments can be used to measure the light reflected from various surfaces. Reflection measurements are especially important for determining objectively the colours of such materials as paints and pigments.

Processing of Electron Spectra

The electron spectral band is described by the following parameters—the wavelength or the wave number of the peak (less commonly, the minimum) of the band, the intensity at the peak and (less commonly) the integral intensity, and the band half-width.

The wavelength of the peak is easy to determine for the narrow bands such as those of benzene (Fig. 12, *1*). There are several techniques for determining the position of the peak for the wide bands with diffuse peaks.

The most widely used technique is to draw a tangent at the spectral band parallel to the x-axis. The tangency point yields λ_{max} or ν_{max} (Fig. 29, *1*). Another technique is to draw a few straight lines parallel to the x-axis which intersect the band contour. A smooth line is drawn through the centres of the segments of the lines inside the band contour and the peak is found as the point of intersection of this line with the band contour (Fig. 29, *2*). Sometimes the position of the band is determined by the centre of the segment parallel to the x-axis passing at the level of half-peak intensity (Fig. 29, *3*). This technique for determining λ_{max} is applicable only to the symmetrical bands. Most spectrophotometers are calibrated in wavelengths, and when converting the measurement results into wave numbers

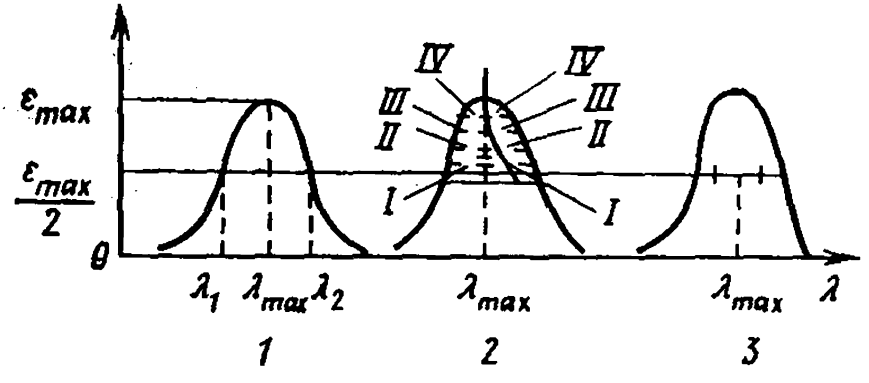


Fig. 29.
The main parameters of the spectral band: *1*, *2*, *3*—techniques for determination of the peak positions.

one should take into account the measurement error. For an СФ-16 instrument this error is 1 nm. For instance, the wave number of the absorption band peak for the aqueous solution of nitrobenzene at $\lambda = 268$ nm is

$$\nu = \frac{1}{\lambda} = 37\,313 \text{ cm}^{-1},$$

$$\Delta\nu = \frac{\Delta\lambda}{\lambda^2} = \frac{1 \cdot 10^7}{268 \cdot 268} \text{ cm}^{-1} = 150 \text{ cm}^{-1},$$

$$\nu = 37\,300 \pm 150 \text{ cm}^{-1}$$

The wave number found from the wavelength should allow for the measurement error.

The band shape is determined by the band half-width and the asymmetry factor. The band half-width $\Delta\nu_{1/2}$ is the distance (on the wavenumber or wavelength diagram) between the points of the spectral curve where intensity is half of the peak intensity (Fig. 29, *1*):

$$\Delta\nu_{1/2} = \nu_1 - \nu_2 \qquad (20)$$

For the structureless electron bands the half-width is of the order of a few thousands of inverse centimetres. For some vibrational electron bands of gases the half-width comes to a few tens of inverse centimetres.

The band intensity is determined from eq. (10). Since the instrument measures transmittance to 1% and the error of the optical density value is 2%, the meaningful value of ε should not be calculated with greater accuracy.

The electron absorption spectra contain bands whose intensities can differ by a few orders of magnitude. To present such bands at the same diagram the log ε values are plotted along the *y*-axis. Thus, a scale of 5 units makes it possible to plot bands differing in intensity by 5 orders of magnitude with the same accuracy. Naturally, these bands should be recorded under different conditions (that is, by varying the concentrations and thicknesses of the samples; see Problem 12, Figs. 22-23).

Exercise 1. Calibration of Spectrophotometer by Wavelengths

To calibrate a spectrophotometer is to determine the correspondence between the wavelength of the light passing through the sample and the reading of the instrument. Calibration is verified directly by visual observation or photoelectrical recording of the spectrum of a mercury-helium lamp.

Equipment: a mercury-helium lamp, 1-cm cell, benzene, a didymium glass plate, and an СФ-4 spectrophotometer.

Operational procedure:

(1) Mount a ДРГС-12 mercury-helium lamp on the spectrophotometer.

(2) Set the slit width of 0.02 nm.

(3) Visual calibration: (a) remove the photodetector chambers and observe the exit slit through the exit of the cell compartment; (b) turning the wavelength knob observe the mercury lines (see below). The wavelength readings of the instrument should coincide with the wavelengths of the mercury lines.

Photoelectric calibration: (a) close the blind; (b) balance the dark current.

(4) Set the readout potentiometer to *x1* and the sensitivity switch to *3*.

(5) Set the readout potentiometer to 10% transmittance.

(6) Open the blind.

(7) Slowly turning the wavelength knob adjust the spectral line to the exit slit (the pointer of the ammeter deflects to the right). Decrease the slit width so that the pointer stays within the dial.

(8) Take the reading of the wavelength dial at the moment of the largest deflection of the pointer (at this moment the pointer starts to deflect to the left). Turning the wavelength knob from lower to higher values repeat these measurements several times and tabulate the results.

The following lines are recommended for calibration in the ultraviolet spectral region—248.2, 253.7, 280.4 and 302.2 nm; the lines at 388.9, 404.7, 435.8, 546.1, 577.0, 587.6 and 1083.0 nm are recommended for the visible and near infrared regions.

Lines useful for calibration are found in the spectrum of benzene vapour which can be easily produced by putting a drop of liquid benzene into a 1-cm cell (236.3, 241.6, 247.1, 252.9 and 258.9 nm).

Filters or glass plates are used for rapid verification of calibration, for instance, the didymium glass (573, 585 685, 740 and 808 nm). However, this verification is less accurate than that with the mercury lamp emission lines or the absorption bands of benzene vapour.

Exercise 2. Verification of the Optical Density Scale Using Standard Solutions

Verification of the optical density scale can be carried out by using standard solutions of certain concentrations prepared from high-purity compounds whose absorption coefficients are known. As the optical density results depend strongly on the band position, the absorption bands of these compounds should not be narrow or steep. The most convenient compounds for this purpose are potassium chromate, potassium dichromate, cobalt ammonium sulphate, potassium nitrate, copper sulphate, and some others.

Equipment: two 1-cm cells and standard solutions.

Operational procedure:

(1) Prepare the standard solutions: (a) to prepare the potassium chromate solution dissolve 0.04 g of K_2CrO_4 in 0.05 N solution of potassium hydroxide, place the solution into a 1-l flask, add the same alkali solution to make 1 l and stir the mixture; (b) to prepare the cobalt ammonium sulphate solution put 14.481 g of $CoSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$

TABLE 10

OPTICAL DENSITIES OF THE STANDARD SOLUTIONS (1-cm thick)

Wavelength (nm)	K_2CrO_4	$(NH_4)_2Co(SO_4)_2$	$CuSO_4$	Wavelength (nm)	K_2CrO_4	$(NH_4)_2Co(SO_4)_2$	$CuSO_4$
215	1.4318	—	—	375	0.9872	—	—
220	0.4559	—	—	380	0.9281	0.0065	0.035
225	0.2218	—	—	385	0.8182	—	—
230	0.1675	—	—	390	0.6840	0.0088	0.0028
235	0.2076	—	—	395	0.5229	—	—
240	0.2933	—	—	400	0.3872	0.0125	0.0023
245	0.3893	—	—	405	0.2840	0.0144	0.0021
250	0.4962	—	—	410	0.1972	0.0168	0.0019
255	0.5719	—	—	420	0.1261	0.0224	0.0016
260	0.6345	—	—	430	0.0841	0.0340	0.0014
265	0.6968	—	—	436	0.0650	0.0437	0.0013
270	0.7447	—	—	440	0.0535	0.0522	0.0012
275	0.7620	—	—	450	0.0325	0.0773	0.0011
280	0.7235	—	—	460	0.0173	0.1031	0.0011
285	0.5952	—	—	470	0.0083	0.1213	0.0012
290	0.4295	—	—	480	0.0035	0.1349	0.0014
295	0.2782	—	—	490	0.0009	0.1472	0.0018
300	0.1518	—	—	492	—	0.1497	0.0019
305	0.0809	—	—	500	0.0000	0.1635	0.0026
310	0.0458	—	—	502	—	0.1661	0.0028
315	0.0434	—	—	510	—	0.1742	0.0038
320	0.0620	—	—	520	—	0.1689	0.0055
325	0.0915	—	—	530	—	0.1452	0.0079
330	0.1457	—	—	540	—	0.1113	0.0111
335	0.2187	—	—	546	—	0.0901	0.0135
340	0.3143	—	—	550	—	0.0775	0.0155
345	0.4202	—	—	560	—	0.0496	0.0219
350	0.5528	0.0038	0.0090	570	—	0.0308	0.0292
355	0.6948	—	—	578	—	0.0219	0.0368
360	0.8297	0.0040	0.0063	580	—	0.0207	0.0390
365	0.9393	—	—	588	—	0.0167	0.0487
370	0.9914	0.0050	0.0046	590	—	0.0158	0.0518

Table 10 (cont.)

Wavelength (nm)	K_2CrO_4	$(NH_4)_2Co(SO_4)_2$	$CuSO_4$	Wavelength (nm)	K_2CrO_4	$(NH_4)_2Co(SO_4)_2$	$CuSO_4$
600	—	0.0137	0.0680	680	—	0.0076	0.392
610	—	0.0124	0.0885	690	—	0.0066	0.459
620	—	0.0115	0.1125	700	—	0.0054	0.527
630	—	0.0112	0.143	710	—	0.0046	0.592
640	—	0.0110	0.180	720	—	0.0038	0.656
650	—	0.0105	0.224	730	—	0.0032	0.715
660	—	0.0097	0.274	740	—	0.0030	0.768
668	—	0.0089	0.319	750	—	0.0028	0.817
670	—	0.0087	0.332				

into a beaker and add distilled water and 10.0 ml of sulphuric acid (density 1.835). Pour the solution into a 1-l flask, add distilled water to make 1 l and stir the solution; (c) to prepare the copper sulphate solution put 20.0 g of copper sulphate $CuSO_4 \cdot 5H_2O$ into a beaker and add distilled water with 10.0 ml of sulphuric acid (density 1.835). Pour the solution into a 1-l flask, add distilled water to make 1 l and stir.

(2) Carefully wash and dry 1-cm cells.

(3) Record the absorption spectra of the solutions in distilled water: copper sulphate—in the 400-750 nm range, potassium chromate—in the 215-500 nm range and cobalt ammonium sulphate—in the 280-750 nm range.

(4) Compare the measured optical density with the data given in Table 10. The results should be identical to 1-2%.

Exercise 3. Determination of the Main Parameters of the Electron Absorption Bands

The following main parameters of the electron absorption bands will be determined: (a) wave numbers of the peaks and minimums ν_{max} and ν_{min} of the absorption bands;

(b) extinction coefficients ε_{max} and ε_{min} at the peaks and minimums; (c) half-widths $\Delta\nu_{1/2}$ of the absorption bands.

Equipment: two cells (from 0.01 to 1 cm, depending on the band intensity), a solution of a known concentration, graph paper, and analytical balance.

Operational procedure:

(1) Record the electron absorption spectrum of a solution with a known concentration with respect to the solvent. Solution of almost any organic compound with the bands in the 210-800 nm range can be used, for instance, potassium chromate (see Exercise 2), *para*-substituted derivatives of benzene (*p*-nitroaniline), etc.

(2) Plot the recorded spectrum in the ε vs. λ and ε vs. ν coordinates (ε is found from eq. (10)).

(3) Determine the values of ν_{max} using the three techniques described above (p. 64, compare them) and the values of ν_{min} for all the bands in the spectrum.

(4) Determine the extinction coefficients ε_{max} and ε_{min} corresponding to the wave numbers found in (3).

(5) Find the half-widths of the absorption bands: $\Delta\nu_{1/2} = \nu_1 - \nu_2$ where ν_1 and ν_2 are the wave numbers for the points of the spectral curve with the extinction coefficient of $\varepsilon_{max}/2$.

Exercise 4. Verification of the Beer-Lambert-Bouguer Law

The Beer-Lambert-Bouguer law (p. 13) is satisfied only when the absorbing particles do not undergo dissociation or any other chemical transformations (association, hydrolysis, etc.) which change the concentration of absorbing centres. Therefore, for all quantitative spectrophotometric analyses there should be verified the applicability of the law to the solvent in the total concentration range being used (the instrumental deviations from the law are discussed on p. 59).

Equipment: a set of demountable cells, aqueous solution of nitrobenzene, measuring cylinders, and pipettes.

Operational procedure:

(1) Record the spectrum of the aqueous nitrobenzene solution (or other solution) in 1-mm, 2-mm, 5-mm, 10-mm and 20-mm cells.

(2) Dilute the starting solution with water by a factor of 2, 4 and 8, and record the spectra of the diluted solutions in 2-mm, 5-mm, 10-mm, 20-mm and 50-mm cells.

(3) Find the optical density D for all the solutions at the absorption band peak.

(4) Plot D as a function of concentration c and find ε for each cell thickness.

(5) Plot D as a function of thickness l and find ε for each concentration.

(6) Compute the standard deviations for the results.

Exercise 5. The Effect of Solvent on Electron Spectra

Solvatochromic effects will be measured for two absorption bands of nitromethane and one of acetone to find the type of the respective electron transitions ($\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$).

Equipment: acetone, nitromethane, ethanol, hexane (spectrally pure).

Operational procedure:

(1) Fill a 1-cm quartz cell with hexane and record its spectrum (fill the reference cell with hexane, too). Verify that the solvent is transparent enough up to 210 nm.

(2) Immerse a glass rod into pure nitromethane and then into the cell and stir hexane. Record qualitatively the spectrum of nitromethane in the 200-300 nm range and find the position of the peak about 210 nm.

(3) Add a drop of nitromethane into the cell, stir the solution and once again record the spectrum. Find the posi-

tion of the band at 270 nm. Compare the relative intensities of these two bands.

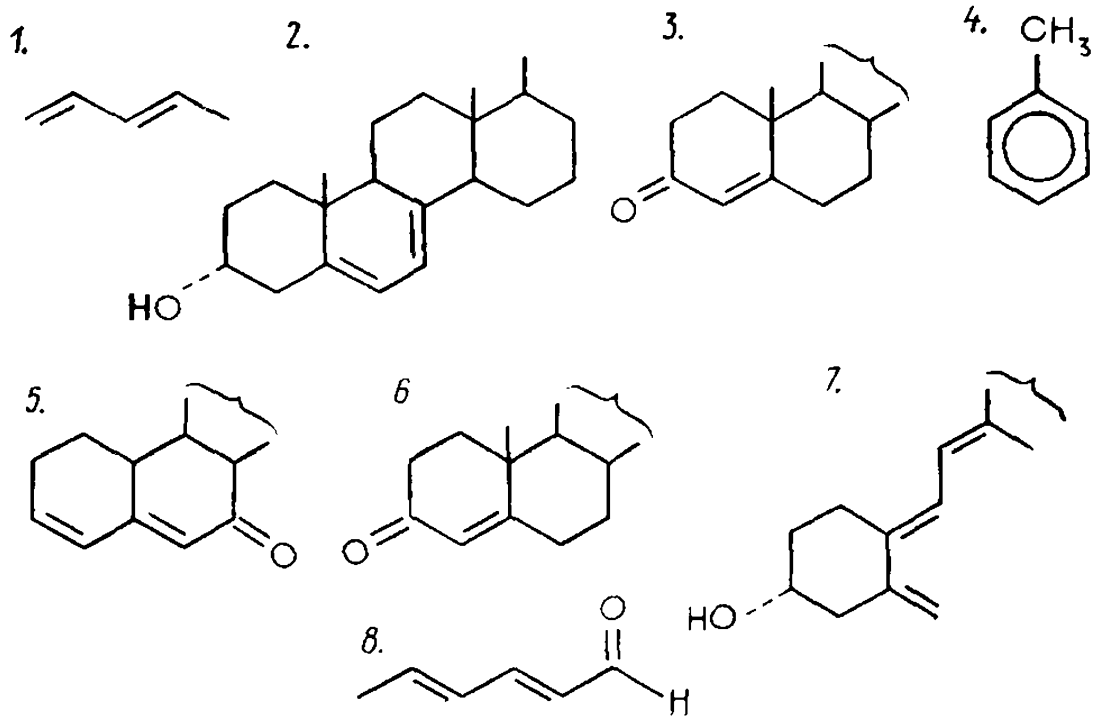
(4) Repeat the procedure with ethanol and water as solvents.

(5) Tabulate the values of λ_{max} for each band in each solvent and determine the type of solvatochromic shift and the type of electron transition.

(6) Analyze the absorption spectrum of acetone in hexane, ethanol and water with the same technique in the 240-300 nm range and determine the type of electron transition.

Exercise 6. Application of Woodward's Rule

Equipment: flasks with ethanol solutions of the following compounds (concentration 10^{-3}-10^{-4} mole/l): piperylene (1), ergosterol (2), 16-dehydroprogesterone (3), toluene (4), $\Delta^{3,5}$-cholestadienone-7 (5), Δ^{4}-androstendione-3,17 (6), vitamin D_3 (7), hexadiene-2,4-al (8):



Operational procedure:

(1) Record the UV spectrum for each solution in the 200-350 nm range using a 1-cm cell (the reference cell is filled with ethanol).

(2) Compare the measured peak wavelengths with the values found from Woodward's rule and identify each solution.

Exercise 7. Determination of the Dissociation Constants for Acids and Bases

The dissociation constants are important parameters describing structures of organic molecules. These constants can be found from variations of the absorption spectra with pH value of the medium.

Dissociation of the acid HB in water can be described by the following equation where B^- is the respective base:

$$HB + H_2O \rightleftarrows H_3O^+ + B^- \tag{21}$$

The mass action law yields for this equilibrium state:

$$K_a = c_{H_3O^+} \cdot \frac{c_{B^-}}{c_{HB}} \tag{22}$$

Taking negative logarithm of eq. (22) we obtain

$$-\log K_a = -\log c_{H_3O^+} - \frac{\log c_{B^-}}{c_{HB}} \tag{23}$$

$$pK_a = pH + \frac{\log c_{HB}}{c_{B^-}} \tag{24}$$

If Beer's law is satisfied, the term c_{HB}/c_{B^-} can be replaced by $D - D_{B^-}/D_{HB} - D$ (here D is the optical density of

the equilibrium mixture) so that we obtain

$$pK_a = \text{pH} + \log \frac{D - D_{B^-}}{D_{HB} - D} \quad (25)$$

Similar equations can be written for the bases:

$$H_2O + B \rightleftarrows HB^+ + OH^- \quad (26)$$

$$pK_a = \text{pH} + \log \frac{D_B - D}{D - D_{HB^+}} \quad (27)$$

The constants pK are determined for several pH values close to pK_a.

Materials: nitroaniline, hydrochloric acid.

Operational procedure:

(1) Prepare 0.001 M nitroaniline solution, pour it into 7 flasks and dilute by a factor of 10 with hydrochloric acid solutions of the following concentrations: 0.0235, 0.0373, 0.0607, 0.0969, 0.1485, 0.2340 and 0.3730 M.

(2) Determine the optical density of these solutions at 270 nm in 1-cm cells.

(3) Find pK from eq. (27) for each solution, taking $D_B = 0.138$ and $D_{HB^+} = 0.693$, and determine the mean value.

Exercise 8. Determination of the Concentration of a Solution

Electron spectrophotometry is widely and successfully applied for determining small amounts of compounds. This exercise consists in recording the spectrum of anthracene and determining its concentration.

Materials: anthracene, hexane.

Operational procedure:

(1) Prepare anthracene solutions in hexane with the concentrations of $0.6 \cdot 10^{-4}$ mole/l and $0.3 \cdot 10^{-5}$ mole/l,

record the absorption spectra in 1-cm cell in the 300-400 and 220-300 nm ranges, respectively, and calculate the extinction coefficients for the characteristic peaks at 250 nm and 320-370 nm.

(2) Measure the optical density of an anthracene solution of an unknown concentration and find the anthracene concentration from eq. (10) using the mean value of ε_{max} from step (1).

Exercise 9. Analysis of Bicomponent Mixtures (for amino acids)

Quantitative determinations of the composition of multicomponent mixtures make use of the additivity of absorption, that is, the total absorption by a mixture is a sum of absorptions by individual components. If Beer's law is satisfied and the extinction coefficients are known for each component, the optical density of a mixture at a given wavelength is given by the following equation:

$$D = (\varepsilon_1 c_1 + \varepsilon_2 c_2 + \ldots) \cdot l \qquad (28)$$

If the mixture contains n components the optical density should be measured at n various wavelengths, and n equations (28) should be written down. This technique is widely used, particularly, for analyzing bicomponent systems. The spectra are recorded at two wavelengths selected so that at one of them the absorption intensities of the components are sharply different and at the other wavelength both components have sufficiently high absorption. Moreover, the selected wavelengths must be at the parts of the spectral curve with small slopes (typically, in the vicinity of the peaks or minimums of the bands) since the accuracy of determination is significantly lower when small variations of the wavelength result in large variations of the optical density. As a typical illustration it is suggested

here to carry out the analysis of a mixture of two amino acids, tyrosine and tryptophan, found in proteins.

Tyrosine and tryptophan exhibit selective absorption in the 220-350 nm range:

Tyrosine: $\lambda_1' = 277$ nm ($\varepsilon_1' = 1500$) in 0.1 *M* HCl,
$\lambda_2' = 294$ nm ($\varepsilon_2' = 2550$) in 0.1 *M* NaOH.

Tryptophan: $\lambda_1'' = 278$ nm ($\varepsilon_1'' = 5500$) in 0.1 *M* HCl,
$\lambda_2'' = 281$ nm ($\varepsilon_2'' = 5000$) in 0.1 *M* NaOH.

The absorption curves for these amino acids intersect at 294 and 257 nm where $\varepsilon' = \varepsilon''$. Then eq. (28) readily yields the sum of molar concentrations:

$$c = c_1 + c_2 = \frac{D}{\varepsilon} \tag{29}$$

When we measure the intensity at another wavelength λ, we shall determine the content of each amino acid in the mixture:

$$c_1 = \frac{D^\lambda - \varepsilon_2^\lambda c}{\varepsilon_1^\lambda - \varepsilon_2^\lambda} \tag{30}$$

The subscript 1 denotes tyrosine and 2 denotes tryptophan (it is suggested that a student independently derive eq. (30)).

Materials: tyrosine, tryptophan, 0.1 *M* HCl, 0.1 *M* NaOH.

Operational procedure:

(1) Record the spectra of tyrosine and tryptophan.

(2) Plot the ε-λ absorption curves for both amino acids and find the intersection points.

(3) Record the spectrum of amino acids and determine the total concentration according to eq. (29).

(4) Select another wavelength for analysis, and calculate the contents of the amino acids.

(5) Determine the measurement error using the known concentrations of tyrosine and tryptophan.

Chapter 2

Infrared Spectroscopy

Infrared spectroscopy is a major modern physical technique for analysis of organic compounds. In contrast to the UV spectra, the IR spectra of most organic compounds contain extensive numbers of absorption bands due to vibrations of almost all chemical groups in compounds. The infrared (IR) spectra are recorded in the 2-50 μm range (5000-200 cm^{-1}).

VIBRATIONS OF MOLECULES

Vibrations and Spectra of Diatomic Molecules

The chemical bond of a diatomic molecule can be described in a simplified form as an elastic spring whose stretching and compression simulate vibrations of atoms in the molecule. For the harmonic oscillator the restoring force is proportional to the displacement of nuclei from the equilibrium position and its direction is opposite to the displacement:

$$f = -K\ \Delta r$$

The coefficient K is known as the force constant of the bond and describes the rigidity of the bond (or elasticity of the bond).

The laws of mechanics yield the following relationship between the frequency ν of the stretching vibration, the

force constant K, and the masses m_1 and m_2 of the atoms in the molecule:

$$\nu = \frac{1}{2\pi} \sqrt{\frac{K}{\mu}} \tag{1}$$

where μ is the reduced mass:

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

The force constants for the single, double and triple bonds are about $(4\text{-}6) \cdot 10^2$, $(8\text{-}12) \cdot 10^2$ and $(12\text{-}8) \cdot 10^2$ N/m, respectively, that is, the ratio is 1 : 2 : 3.

Eq. (1) shows that the vibration frequency increases with increasing bond strength (bond multiplicity) and decreasing atom masses. Using eq. (1) we can estimate the ranges of variation of the vibration frequencies. For instance, for the group C≡N the frequency is about 2250 cm^{-1}, for the group C=N it is about 1650 cm^{-1} and for the group C—N it is about 1050 cm^{-1}. Here the variation of the frequency is due to the decreasing force constant of the C—N bond, the atom masses being the same.

Assuming that vibrations in a diatomic molecule are harmonic to the first approximation so that the molecule can be described by a harmonic oscillator we find that the total vibration energy should satisfy the quantum condition:

$$E_v^{\text{vibr}} = \left(v + \frac{1}{2}\right) h\nu_0 \tag{2}$$

where v is the vibrational quantum number ($v = 0, 1, 2, 3, \ldots$) and ν_0 is the frequency of the ground state vibration (the fundamental frequency) given by eq. (1).

Eq. (2) yields a system of equally spaced energy levels (Fig. 30). It should be noted that $E^{\text{vibr}} \neq 0 \left(E_0 = \frac{1}{2} h\nu_0\right)$ when $v = 0$. This means that the nuclei in molecules never cease to vibrate and even at the lowest vibrational state

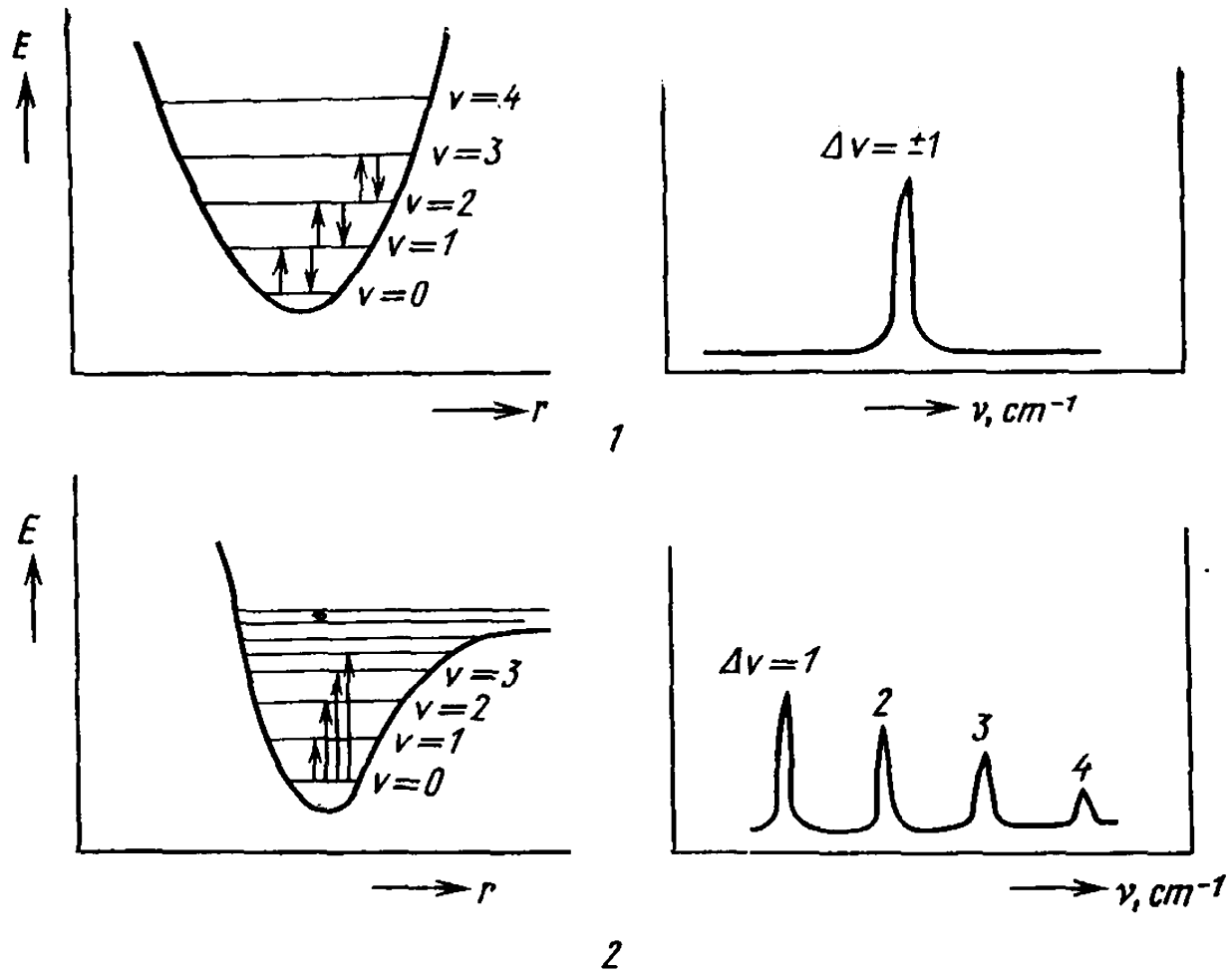


Fig. 30.
The potential curves, energy levels and schematic spectra of a harmonic (1) and an anharmonic oscillator (2).

the molecule possesses some vibrational energy. When the molecule absorbs a radiation quantum $h\nu$ it goes over to a higher energy level. The difference in energies of the levels equals the energy of the absorbed quantum:

$$h\nu = E_{v+1} - E_v \tag{3}$$

At the same time eq. (2) yields the following expression for the difference between two energy levels:

$$E_{v+1} - E_v = h\nu_0 \tag{4}$$

Comparison of eqs. (3) and (4) shows that the frequency ν of the absorbed radiation quantum is identical to the funda-

mental frequency ν_0 (wave number) given by eq. (1). Thus, the spectrum of the harmonic oscillator contains one line or band at the frequency ν_0 which is the natural frequency of the oscillator (Fig. 30, *I*). At room temperature most molecules are, typically, at the ground vibrational state since the thermal excitation energy is considerably lower than the energy of transition from the ground state to an excited state. Therefore, it is easier to observe in the experiments the transitions from the ground vibrational state ($v = 0$) to the first excited state ($v = 1$). Other transitions changing the quantum number by 1, that is, the transitions between neighbouring levels, are possible in the harmonic oscillator:

$$\Delta v = \pm 1 \tag{5}$$

The recorded infrared absorption bands of the gas molecules have complex structures since each vibrational state of an individual molecule has its system of rotational sublevels.

To analyze the recorded spectra let us discuss a system of two vibrational levels and the respective rotational sublevels.

Fig. 31 shows schematically a band due to a change in the vibrational-rotational state of a molecule. When a molecule absorbs radiation quantum it goes over to the neighbouring vibrational level and to another rotational sublevel, and the variation of the rotational quantum number ΔI can be not only $+1$ but also -1. The first transition gives rise to the so-called *R* branch which lies at higher frequencies with respect to the band centre, and the second transition gives rise to the *P* branch of the vibrational-rotational band.

The condensed phases have vibrational bands lacking any rotational structure, that is, the bands are due to purely vibrational transitions.

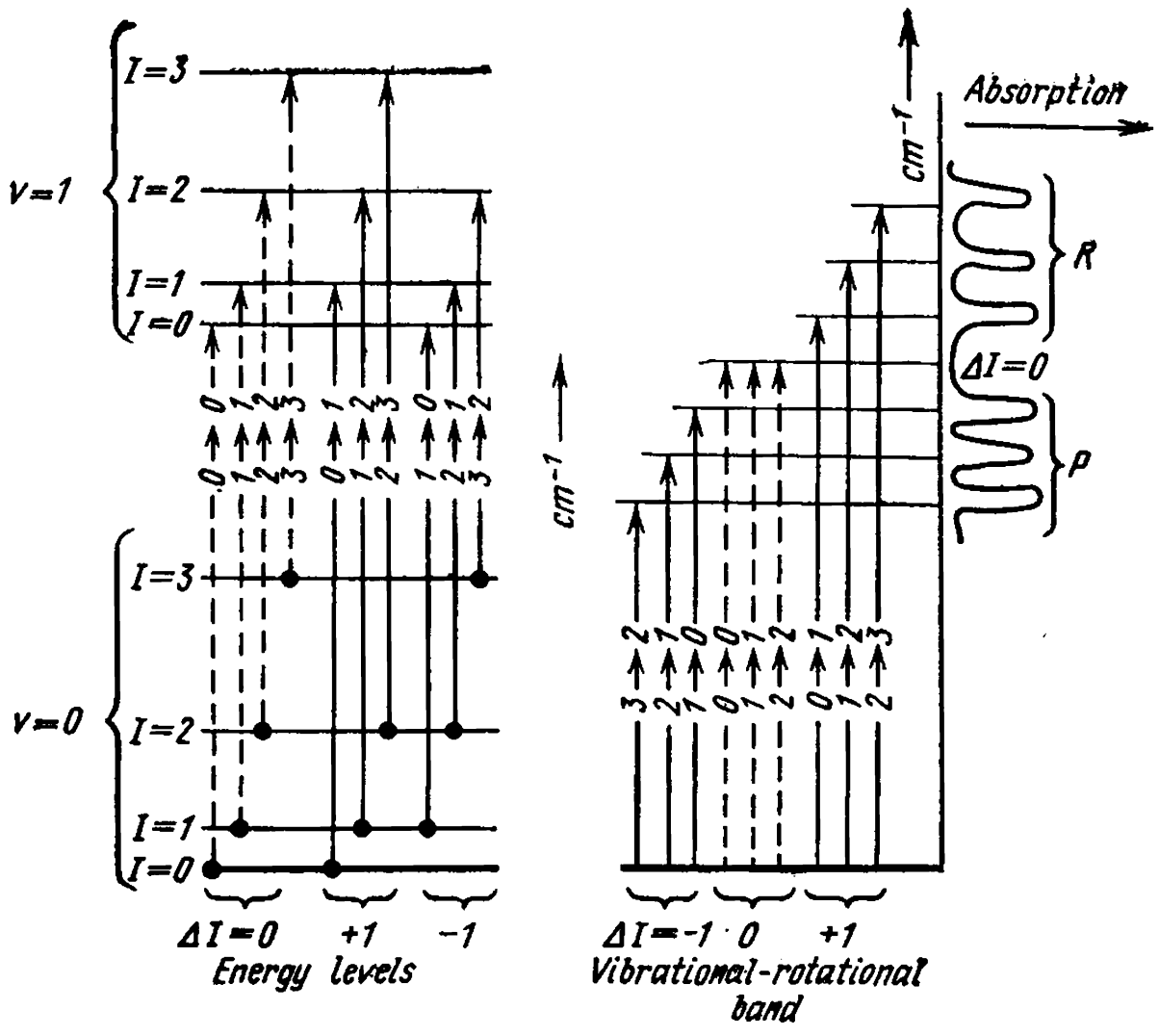


Fig. 31.
The system of levels giving rise to the rotational-vibrational spectrum.

We have analyzed the harmonic oscillator which is an idealized model of a diatomic molecule. The typical molecular vibrations are more or less anharmonic. Fig. 30, *2* presents the potential energy curve for the diatomic molecule showing that vibrations can be treated as harmonic only for small vibrational quantum numbers v. The anharmonic oscillator can have transitions with $\Delta v = \pm 1, \pm 2, \pm 3$, etc., besides the transitions between the neighbouring levels, so that the spectrum can contain overtones with the frequencies $2\nu_0$, $3\nu_0$ and so on, with decreasing intensity (Fig. 30, *2*). The overtone intensities are considerably lower

than the intensity of the fundamental vibration ($\Delta v = 1$), for instance, the intensity of the first overtone is 1-10% of the intensity of the fundamental vibration. The intensities of the subsequent overtones are much lower so that for many molecules the third or fourth overtones are impossible to record. With increasing v the distance between the neighbouring vibrational levels decreases, and for a certain maximum number v_{max} the energy of the molecule comes to the limit E_{max} which is equal to the dissociation energy.

Vibrations and Spectra of Polyatomic Molecules

The number of possible types of vibrations rapidly increases with increasing number of atoms in the molecule, so that the vibrations in polyatomic molecules are much more complex than those in diatomic molecules. The full vibrational spectrum of a polyatomic molecule consists of a large number of bands and lines reflecting all the characteristics of its complex vibrational-rotational motion.

Generally, a molecule of N atoms has $3N - 6$ basic vibration types for a nonlinear molecule and $3N - 5$ for a linear one. Thus, a diatomic molecule ($N = 2$) has one vibration type ($3 \cdot 2 - 5 = 1$), a triatomic molecule has 3 (nonlinear) or 4 (linear) vibration types while benzene C_6H_6 has 30 vibration types ($3 \cdot 12 - 6$). Owing to this fact interpretation of the IR spectra of polyatomic molecules is far from being easy.

Vibrations of different atoms in the molecule interact between themselves so that a complex molecule can be treated as a set of interacting oscillators. The energy of one oscillator (one bond in the molecule) is fairly rapidly distributed over other bonds, so that all atoms and bonds are involved in the vibration. Any complex vibration can be decomposed into simple, so-called normal* vibrations.

* The normal vibrations are the molecular vibrations when all the nuclei vibrate with the same frequency and phase.

It should be noted that the number of the normal vibrations for a molecule equals the number of the vibration types possible for the molecule. The frequencies found in the molecular spectra are just the frequencies of the fundamental normal vibrations and their overtones.

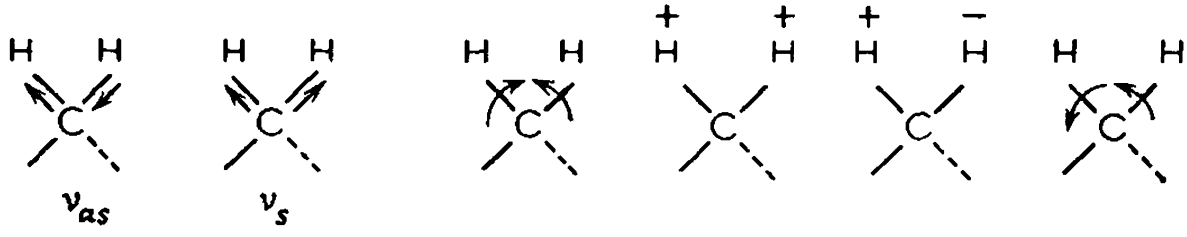
A natural question is whether a certain vibration frequency can be attributed to a given chemical bond. If this could be done, the spectral data could be used to identify bonds and groups in complex molecules. Rigorous assignment of the IR absorption bands to certain chemical groups can be done only by theoretical analysis which is a labour-consuming task, particularly, for complex molecules. As mentioned above, measurements yield the frequencies of normal vibrations. If for a given normal vibration the amplitude of vibration of one bond is much larger than those of all the other bonds, this normal vibration frequency can be assigned to this bond. Then this normal vibration is known as the characteristic vibration for this bond. Naturally, the number of absorption bands is not equal to the number of normal vibrations since if the vibration does not change the dipole moment of the molecule, it does not absorb infrared radiation (is not infrared active) and no relevant infrared absorption band is found in the spectrum. It should be noted that infrared activity is exhibited only by those molecules which change their electric dipole moment μ during vibration, that is, if $d\mu/dq \neq 0$ where q is the vibrational coordinate. Therefore, vibrations of such molecules as hydrogen chloride, methane, benzene, etc. give rise to infrared absorption bands while molecules of hydrogen, oxygen, nitrogen, etc. exhibit no activity.

All molecular vibrations can be classified into two groups—the stretching vibrations and deformation vibrations. If a vibration involves mainly variation of the distance between atoms, with negligible variation of the angles between bonds, the vibration is known as the stretching vibration (ν). If the angles between bonds vary while the lengths of the

bonds remain practically the same, such vibration is known as the deformation vibration (δ, γ)*.

The deformation vibrations require less energy than the stretching vibrations of the same bond, and their absorption bands are found at lower frequencies. The stretching vibrations can be symmetric and asymmetric (ν_s and ν_{as}) while the deformation vibrations can be of the bending, twisting, rocking, wagging, and other types.

The above vibration types can be used to describe vibrations of individual chemical groups as illustrated below by vibrations of the methylene group**:



Stretching vibrations

Deformation vibrations: bending (scissoring), rocking, twisting and wagging

Besides the vibration frequency a very important parameter of the IR spectra is the band intensity, which yields additional valuable information on the molecular structure. The absorption intensity is measured using the integral intensity

$$A = 2.3 \int_{\nu_1}^{\nu_2} \varepsilon d\nu \qquad (6)$$

---

* It should be noted that classification into stretching and deformation vibrations is somewhat arbitrary as the stretching vibrations result in some deformations of angles while the deformation vibrations cause some changes in the bond lengths.

** The plus and minus signs denote vibrations perpendicular to the plane of the page.

where ε is the absorption coefficient and ν_1 and ν_2 are the limits of integration. The integral absorption for the i-th normal vibration depends on the electron parameters of molecules:

$$A_i = \frac{N\pi}{3c}\left(\frac{d\mu}{dq_i}\right)^2_{q_i=q_{i0}} \quad (7)$$

Here N is the Avogadro number, μ is the dipole moment of the molecule, c is the velocity of light, q_i is the normal coordinate for the i-th normal vibration, and q_{i0} is the normal coordinate for the equilibrium state.

It may be assumed that the larger the variation of the dipole moment of the bond during vibration the higher the intensity of infrared absorption. The stretching vibration involves displacement of the negative and positive charges. Therefore, the integral absorption intensity must be enhanced by the factors increasing the electron density for such bonds as C=C, C≡N, N=O, P=O, etc. and reduced by the factors decreasing the electron density.

The experimental results show that the integral intensity of the IR absorption bands increases with decreasing frequency of the stretching vibrations. This is usually attributed to the fact that the vibration frequency itself is a function of the force constant of the bond (eq. (1)) while an increase in the electron density of the bond (and, hence, an increase in the integral intensity of absorption) leads to a decrease in the bond multiplicity (an increase in the bond length).

Hence, each band of the IR spectra has the following characteristics:

1. Peak vibration frequency ν (cm^{-1}).
2. Peak intensity $\varepsilon = D/cl$ (l/mole·cm).
3. Band halfwidth $\Delta\nu_{1/2}$ equal to the band width (cm^{-1}) at the level where the optical density is half of the maximum.
4. Integral intensity A equal to the shaded area of the ε vs. ν (cm^{-1}) plot (see Fig. 32).

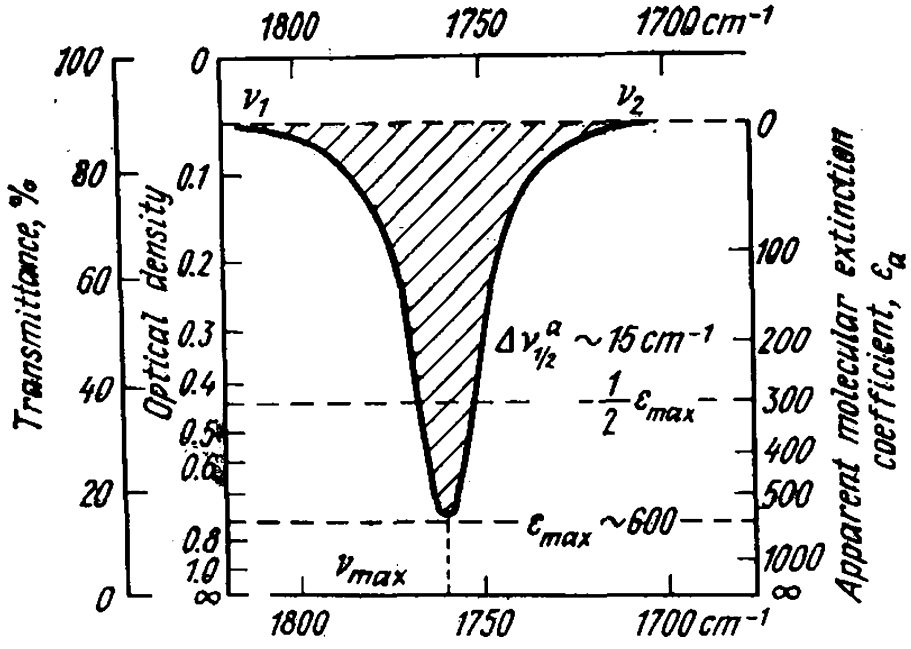


Fig. 32.
The parameters of infrared absorption band.

The IR absorption band (C=0) shown in Fig. 32 has the following parameters:

1. $\nu = 1760$ cm^{-1}.
2. $D_{max} = 0.77$, $\varepsilon = 600$ l/mole·cm.
3. $\Delta\nu_{1/2} = 15$ cm^{-1}.
4. $A \cdot 10^{-4} = 1.34$ l/mole·cm^2.

MAIN APPLICATIONS OF INFRARED SPECTROSCOPY TO SPECTROCHEMICAL ANALYSIS

Chemical applications of IR spectroscopy require profound understanding of the main features of the IR spectra to assign bands to the appropriate structural elements of the molecules and to account for the effect of various factors on variation of frequencies and intensities. The IR spectroscopy has a very wide range of applications—identification of compounds, analysis of group structures, quantitative analysis, studies of intramolecular and intermolecular

interactions, identification of molecular configurations, studies of reaction kinetics, etc.

Here we shall discuss mainly interpretation of spectra and relationships between the spectra and the structures of organic molecules. We shall limit ourselves to the intermediate IR range between about 3700 and 600 cm^{-1}, since the absorption bands for the principal groups of the organic molecules are found just in this range.

Identification of Compounds and Group Structural Analysis

The IR spectrum is a sensitive characteristic of a compound; it can be used as a criterion for determining whether two compounds are identical or not since each compound has its own absorption spectrum, particularly, in the "fingerprints" range (1300-700 cm^{-1}). In this frequency range even small variations of the compound structure produce significant changes in the IR spectrum. The IR spectrum can be used for identification of a newly synthesized compound as it evidences the presence (or lack) of certain groups of atoms.

The fact that various chemical groups have their own characteristic frequencies makes possible determinations of the structural features of chemical compounds.

Theoretical predictions and experimental results show, that many fundamental bands in spectra of various compounds are in approximately the same spectral ranges (see Fig. 33) and they can be assigned to vibrations of certain atom groups which are relatively little affected by the neighbouring atoms and molecular bonds. The main characteristic frequencies are summarized in the Appendix (Table 1). It can be seen from the table that all normal hydrocarbons have a number of bands in the 2800-3100 cm^{-1} range, produced by the stretching vibrations of the C—H

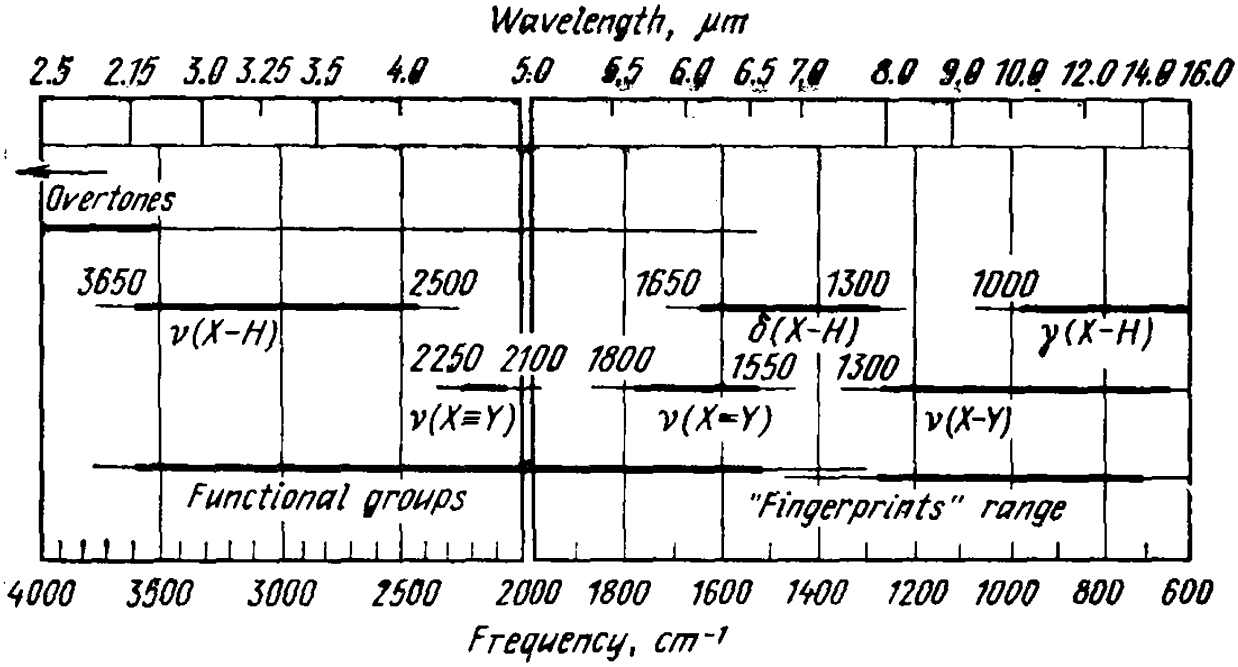


Fig. 33.
The frequencies of the IR spectrum: ν—stretching vibrations, δ—deformation (in-plane) vibrations, γ—deformation (out-of-plane) vibrations.

bonds in the CH, CH_2 and CH_3 groups. The following examples of the characteristic absorption bands can also be given: C=C, C=N (~1650 cm^{-1}), C≡C (~2200 cm^{-1}), C=O (~1725 cm^{-1}), NO_2(ν_{as} ~ 1550 cm^{-1} and ν_s ~ ~ 1340 cm^{-1}), SO_2 (ν_{as} ~ 1300 cm^{-1} and ν_s ~ 1100 cm^{-1}), P=O (~1200 cm^{-1}), OH (~3600 cm^{-1}), NH (~ 3400 cm^{-1}), etc.

Thus, the structure of a compound can be identified from the characteristic absorption frequencies, supported by the results of elemental analysis and other chemical data. Given below are a few examples illustrating analysis of infrared spectra for the organic compounds of various types. Identification of spectrum necessitates full assignment of the absorption bands to chemical groups comprising the molecule, making use of the tables of characteristic frequencies.

For instance, Fig. 34 presents the IR spectrum for the compound with the empirical formula $C_2H_3NO_2$. The for-

mula shows that the compound is unsaturated and can contain a nitro or a nitrite group. If the compound contains the nitrite group (CH_2=CH—O—N=O) in the spectrum there must be one high-intensity band produced by vibration of the N=O band with ν = 1680-1650 cm^{-1} (*trans*-form) or ν = 1640-1625 cm^{-1} (*cis*-form). The spectrum of the nitro group must contain two high-intensity bands due to antisymmetric and symmetric stretching vibrations. The spectrum contains the band of the double bond $\nu_{C=C}$ = = 1640 cm^{-1} and high-intensity bands with ν = 1540 cm^{-1}

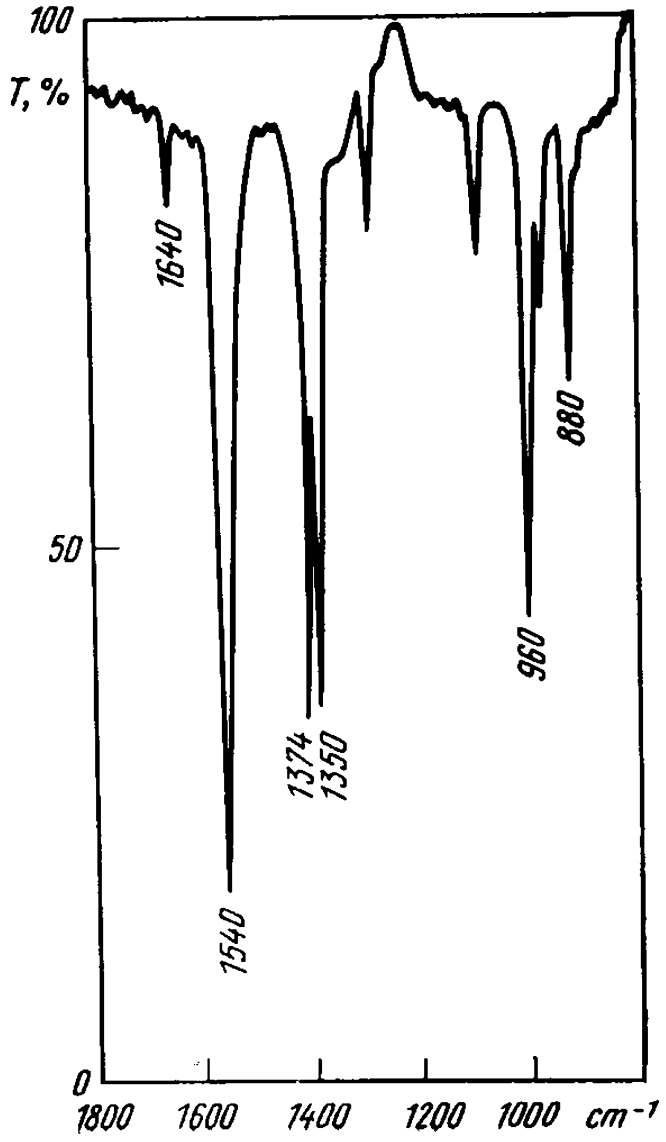


Fig. 34.
IR spectrum of the compound $C_2H_3NO_2$.

and 1350 cm^{-1} which are the characteristic bands of the conjugated nitro group. Other bands in the spectrum are due to the deformation vibrations: 1374 cm^{-1}—δ_{CCH}, 960 cm^{-1}—δ_{HCH}, 880 cm^{-1}—γ_{C-N}. Thus, the compound can be assigned the structure of nitroethane $CH_2=CHNO_2$. Interpretation of spectra should take into account not only the positions of the bands but also their intensities. The absorption bands of the double bonds have typically much lower intensities than those of the polar groups; this can be seen in the above example, too.

Interpretation of the spectra of the relatively simple mono- and disubstituted derivatives of benzene typically presents no difficulties. The benzene ring is best identified by the stretching bands $\nu_{CH} \approx 3030$ cm^{-1} and $\nu_{C=C}$ at 1600-1500 cm^{-1} while the number and positions of the substituents at the ring are typically determined from the bands in the 1000-650 cm^{-1} range. This range can be of great use for group structural analysis. For instance, let us determine the structure of the compound C_7H_7Br whose spectrum contains bands at 3020, 2938, 2918, 1600, 1493, 1452, 1215, 1110, 1072, 1013 and 801 cm^{-1}. It should be borne in mind that if the spectrum contains a stretching band characteristic of a certain group of atoms it is necessary to find the bands due to other types of vibrations of this group to make positive identification of the group. In the spectrum under consideration the bands at 3020, 2938 and 2918 cm^{-1} evidence the presence of C—H bonds of the aromatic ring; this conclusion is supported by the presence of the absorption bands characteristic of the benzene ring (at 1600 and 1493 cm^{-1}). Thus, the spectrum can be interpreted using the table of characteristic frequencies (see Table 11).

Thus, the spectral data suggest that the compound under consideration has a benzene ring with the CH_3 group and a bromine atom at 1,4-positions. Thus, the compound is *p*-bromotoluene.

TABLE 11

ASSIGNMENT OF THE ABSORPTION BANDS FOR THE COMPOUND C_7H_7Br

ν (cm^{-1})	Assignment
3020	C—H stretching vibration in the aromatic ring
2938, 2918	C—H stretching vibration in the alkyl groups CH_3, CH_2, CH
1600, 1493	C=C stretching vibration in aromatic compounds
1452	C—H deformation vibration in the group C—CH_3, δ_{as}
1395	C—H deformation vibration in the group C—CH_3, δ_s
1215, 1110, 1072, 1013	In-plane C—H deformation vibration in 1,2- or 1,4-disubstituted benzene derivatives
801	Out-of-plane C—H deformation vibration in 1,4- or 1,2,3,4-substituted benzene derivatives

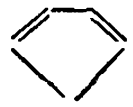
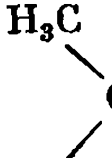
Interpretation of spectra is not always so simple. The spectral bands can overlap, and the overtones of the fundamental frequencies may complicate the picture. Moreover, the absorption bands of a group can be markedly shifted owing to a number of factors—not only those that change the force constants of the bonds (induction effect, conjugation effect, field effect) but also the effect of masses, variation of the valence angles, variation of the force constants of the neighbouring bonds, etc. Thus, though the characteristic band is a fundamental concept of spectroscopy it is very importat to take into account possible deviations from characticity owing to the effect of various (intramolecular and intermolecular) factors which shift the absorption bands. The extent of deviation from character-

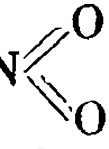
icity describes the variation of the properties of an atom group under the effect of other groups and bonds in the molecule.

Let us discuss the variations in the vibrations of the nitro group caused by the substituents at the α and β positions with respect to the nitro group. Table 12 shows that the characteristic frequencies vary in a fairly wide range.

TABLE 12

THE FREQUENCIES OF THE STRETCHING VIBRATIONS OF THE NITRO GROUP IN VARIOUS NITRO-COMPOUNDS

Compound	ν_{as} (cm^{-1})	ν_s (cm^{-1})	$\Delta\nu$ (cm^{-1})	Compound	ν_{as} (cm^{-1})	ν_s (cm^{-1})	$\Delta\nu$ (cm^{-1})
CH_3NO_2	1578	1390	188		1520	1320	200
	1568	1373	195	$CH_3CH(NO_2)_2$	1580	1330	250
				$CH(NO_2)_3$	1600	1300	300
	1540	1350	190				

For instance, in nitromethane the ν_{as} and ν_s frequencies are 1578 and 1390 cm^{-1}; they can be regarded as the characteristic frequencies of the bond  in the absence of any noticeable interaction with other bonds. Conjugation of the nitro group with π-electron systems results in a regular decrease of the frequencies ν_{as} and ν_s while increasing number of nitro groups in the molecule results in a considerable increase in ν_{as} and a decrease in ν_s. The decrease of the frequencies in the first example is due to the π-electron effect producing an excess electron density at the oxygen atoms of the nitro group.

The excess electron density reduces the strength of the N—O bond. The shifts of characteristic frequencies in the CH_3NO_2-$CH(NO_2)_3$ series are caused by variation of the force parameters of the nitro groups. For instance, an increase in the number of nitro groups at the carbon atom changes the orders of the bonds N—O and C—N in the group C—NO_2: the order of the N—O bond increases and the order of the C—N bond decreases so that the difference $\Delta\nu$ increases.

The compounds containing the carbonyl group are, typically, easy to identify as the carbonyl absorption band has an extremely high intensity (ε = 300-2000 in the 1800-1650 cm^{-1} range). The position of the absorption band for the stretching vibrations of the carbonyl group is determined by the character of its double bonding and also by a number of additional factors (the geometry of the molecule, the masses of the atoms, the induction and mesomeric effects, steric factors, etc.). Table 13 presents frequencies and intensities ($\nu_{C=O}$, A) of the absorption bands of the

TABLE 13

FREQUENCIES AND INTENSITIES OF THE CARBONYL ABSORPTION BANDS

Substituent R	$C_6H_5-C(=O)-R$	
	ν (cm^{-1})	$A \cdot 10^{-4}$ (red. units)
H	1715	1.9
CH_3	1680	2.2
Cl	1810	2.5
OCH_3	1732	2.9
OH	1700	5.1
$N(CH_3)_2$	1660	7.4

carbonyl-containing compounds which show that the donor substituents OH and $N(CH_3)_2$ decrease the frequency $\nu_{C=O}$ (compared to R = H) while the acceptor substituent Cl increases this frequency. This effect is explained by the fact that if R is OH the electron density at the C=O bond is higher than if R is Cl.

The integral intensities of the carbonyl absorption bands for the groups given in Table 13 steadily increase. The highest intensity $A_{C=O}$ is found when the substituent R is the amide group since in this case the electron density at the oxygen atom is high.

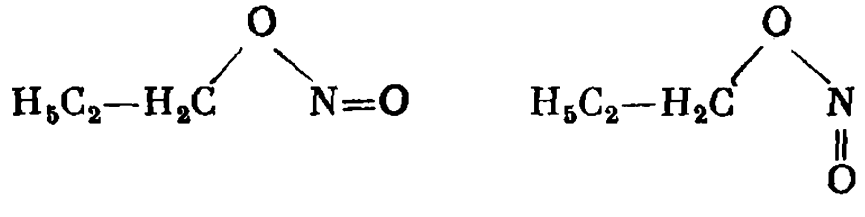
Hence, the intensity of the IR absorption bands can be used as an approximate quantitative measure of the ionicity of a chemical bond. Thus, the absorption band frequencies and intensities yield information on intramolecular interactions, that is, ultimately on the nature of the chemical bonds. However, it should be kept in mind that the absence of bands characteristic for some groups (such as C=C, C≡C, C≡N) cannot always be an evidence of their absence in the molecule owing, typically, to its symmetry. For instance, the absorption band characteristic of the triple bond (2100 cm^{-1}) is not found in the spectra of the symmetrically substituted acetylenes; this fact can be useful for determining the position of the triple (or double) bond.

Configuration of Molecules

Successful identification of geometric isomers by means of chemical analysis is extremely difficult whereas molecules with different spatial arrangements of groups have different absorption spectra.

For instance, the spectrum of propyl nitrite contains two distinct absorption bands, $\nu_{N=O}$ at 1620 and 1660 cm^{-1},

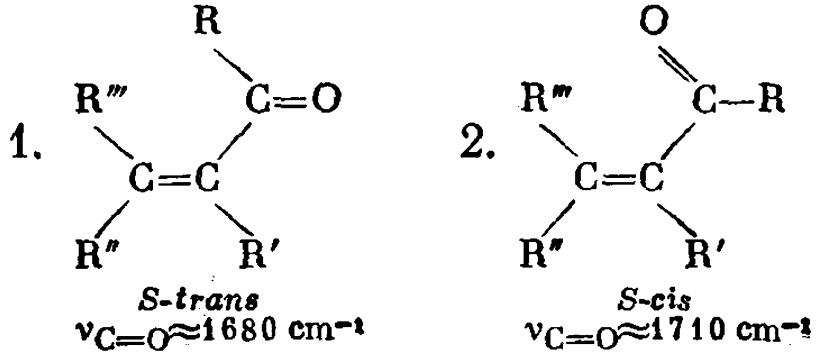
due to two conformations of the molecule:



S-trans $\nu = 1660\ cm^{-1}$ *S-cis* $\nu = 1620\ cm^{-1}$

The ratio of the isomers depends on the temperature; with decreasing temperature the conformations are "frozen" and increasing intensity is observed for the band which has a lower intensity at normal temperature.

The α, β-unsaturated ketones are also known to have two conformations with respect to the double bond:



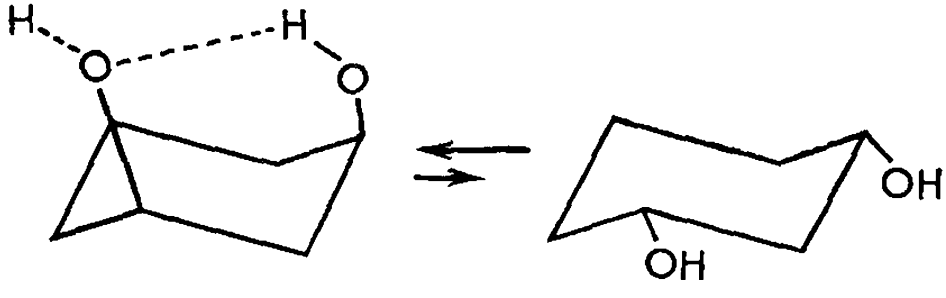
S-trans $\nu_{C=O} \approx 1680\ cm^{-1}$ *S-cis* $\nu_{C=O} \approx 1710\ cm^{-1}$

When the substituents R are not bulky the bonds $\diagdown C{=}C$ and $\diagdown C{=}O$ for the conformation (1) are parallel and for the conformation (2) are not parallel. Hence, the double bond in the conformation (2) has a higher polarization owing to the field effect of the group C=O so that the intensity of its band is higher and the intensity of the band $\nu_{C=O}$ is considerably lower than that of the respective bands in the spectrum of the conformation (1). The intensities of the carbonyl bands of the compounds in the *S-cis*-form are almost always less than half of the intensities of the same bands of the compounds in the *S-trans*-form. The

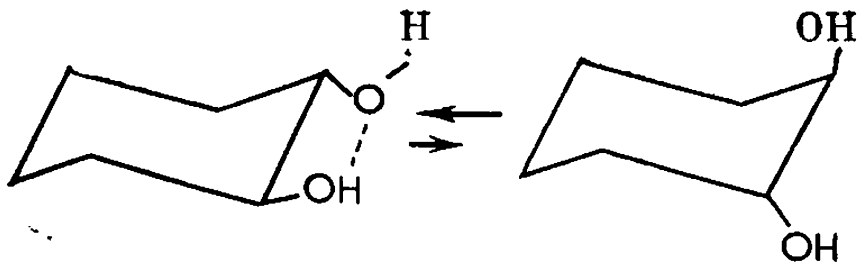
experiments have shown that in stereochemical analysis of the α, β-unsaturated ketones the most useful criterion is the ratio $A_{C=O}/A_{C=C} = r_i$ between the intensities of the bands of the carbonyl group and the double bond. For the *trans*-conformation r_i is 6 to 9 while for the *cis*-conformation r_i is considerably lower and varies from 0.6 to 3.5. Such a large difference in values of r_i makes it possible to use this parameter for fairly accurate determination of the content of isomers. However, deviations from these rules can occur owing either to the steric effects decreasing the degree of conjugation, or to the effect of polar groups.

Let us discuss another example. The IR spectra of 1,3-cyclohexandiol and 1,2-cyclohexandiol have a broad high-intensity band ν_{OH} at 3450 cm^{-1}. The position and intensity of this band for both compounds are practically not changed by dilution with carbon tetrachloride. What can be said about the nature of the vibration ν_{OH} and the stereochemical properties of these two compounds?

The frequency of 3450 cm^{-1} for the band ν_{OH} suggests hydrogen bonding. As the bonding is not affected by dilution the compounds may be chelates. Thus, we can suggest the conformations of *cis*-1,3-cyclohexandiol and *trans*-1,2-cyclohexandiol. Furthermore, a diaxial conformation should be suggested for the first compound and diequatorial conformation for the second compound since these two conformations are the most favourable ones for chelate formation:



cis-1,3-cyclohexandiol

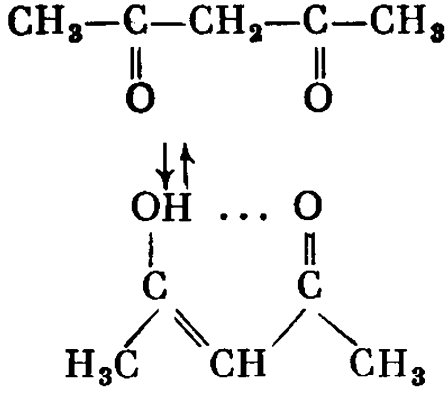


trans-1,2-cyclohexandiol

Current studies of the polysaccharide configurations make use of the IR spectral data. The IR spectra of free monosaccharides show the difference between the absorption spectra of α- and β-isomers both for free monosaccharides and for their methylglycosides, phenylglycosides and acetates.

Tautomerism of Molecules

Some compounds can have various molecular forms and the ratio of these forms depends on the ambient conditions. As each molecular form has its own absorption spectrum any change in the ratio of the molecular forms due to variation of temperature or concentration or due to interaction with the solvent must affect the spectrum of the mixture. For instance, for acetyl acetone we have



$\nu_{C=O} = 1730\ cm^{-1}$

$\nu_{C=O} = 1680\ cm^{-1}$

$\nu_{C=C} = 1640\ cm^{-1}$

In the spectrum of acetyl acetone the carbonyl band is split into two bands—one high-intensity band at 1680 cm^{-1}

and another at 1730 cm^{-1} with lower intensity forming a hump on the wing of the former one. The band at the lower frequency is due to vibration of the C=O group involved in the hydrogen bond. The ratio of the intensities of these two bands provides the information about the content of each form of the compound. The existence of the enol form is also confirmed by the presence of the bands $\nu_{C=C}$ (1640 cm^{-1}) and ν_{OH} (3400-3200 cm^{-1}).

Hydrogen Bond

Infrared spectroscopy is a major experimental technique for identification and analysis of the inter- and intramolecular hydrogen bonds since formation of the hydrogen bond generally shifts absorption bands to lower frequencies, increases the intensity and widens the band caused by the stretching vibration of the group involved in formation of the hydrogen bond. The frequency shift ($\Delta\nu = \nu_{free} - \nu_{bond}$) is often regarded as a measure of the strength of the hydrogen bond. Hydrogen bond at the hydroxyl groups causes the largest shift of the band of the stretching vibration (ν_{OH}) so that a narrow high-intensity band at 3600 cm^{-1} of the free hydroxyl group is replaced by a wide high-intensity band in the 3400-3200 cm^{-1} range. For very strong hydrogen bonds for instance, in carboxylic acids, the bands of the bound OH group can be displaced to 2600-2500 cm^{-1}. Formation of the hydrogen bond results in lengthening of the bonds O—H, N—H, etc., that is, in reduction of their elasticity; hence, the frequency of the respective stretching vibration decreases (in the 3600-3200 cm^{-1} range). The bands of deformation vibrations are less sensitive to hydrogen bonding which results in a slight increase in the frequency of deformation vibrations δ_{OH} (in the 1400-1250 cm^{-1} range). The polar bond C—O gives rise to a high-intensity absorption band in the 1200-

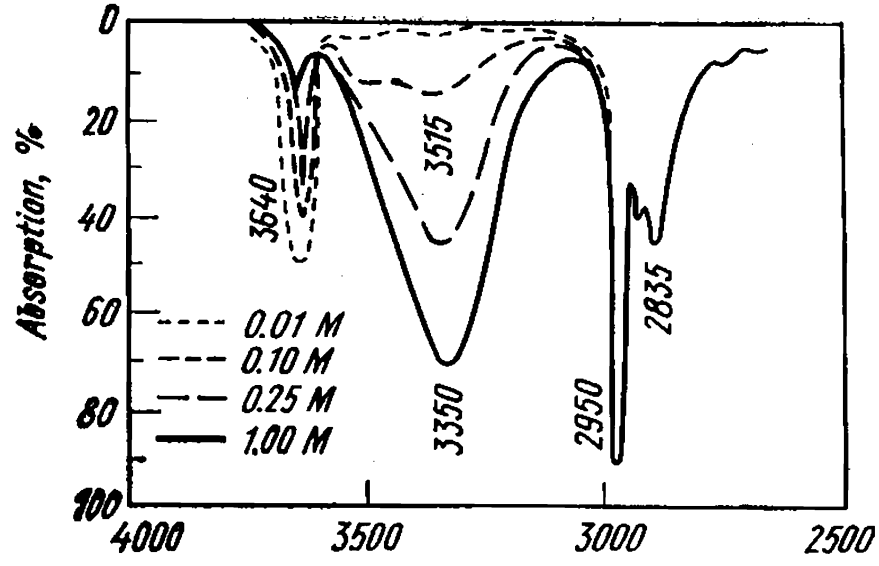


Fig. 35.
IR spectra of carbon tetrachloride solutions of ethanol with various concentrations.

1400 cm^{-1} range which is due to the involvement of this group in the skeletal vibrations.

In the studies of the hydrogen bond, spectra are typically recorded several times for various concentrations of the compound in a nonpolar solvent. Fig. 35 presents the spectra of ethanol in carbon tetrachloride. At low ethanol concentration the stretching vibration of the OH group gives rise to a narrow band at 3640 cm^{-1}, that is, no hydrogen bond is found. At higher ethanol concentrations the spectrum contains a wide band at 3400 cm^{-1} which is due to vibration of the OH groups involved in hydrogen bonding. With increasing ethanol concentration the intensity of the band at 3640 cm^{-1} due to the free OH groups decreases while that of the band due to the bound OH groups increases. Similar effects can be observed in solutions of many amides—a narrow band at 3465 cm^{-1} due to the free NH groups with increasing concentration is being replaced by the band at 3300 cm^{-1} due to the bound NH groups.

In contrast to the intermolecular hydrogen bond, the intramolecular hydrogen bond is not affected by concentration as it is a property of an individual molecule.

The IR spectroscopic techniques are applied for analyzing the structures of proteins and polypeptides. The IR spectra of proteins show the patterns typical of hydrogen bonding (for the NH groups). For instance, no polyglycine exhibits absorption above 3330 cm^{-1}; this fact suggests that all NH groups are capable of hydrogen bonding in the crystalline state.

An increase in temperature, that is, in the velocity of molecular motion, results in rupture of hydrogen bonds. The solvents also affect hydrogen bonding. The solvents containing electronegative atoms (typically, oxygen) form hydrogen bonds themselves.

We have discussed here only a few examples of practical application of the IR spectroscopy for determination of the structures of organic compounds.

This technique, of course, cannot be universal, and the increasingly common current practice is to use for analyzing the structure of compounds a combination of various physical and physico-chemical techniques.

The problems given in this chapter will help in mastering the fundamental skills in using IR spectroscopy for identification of molecular structure and evaluating the scope of its applications.

PROBLEMS IN IR SPECTROSCOPY *

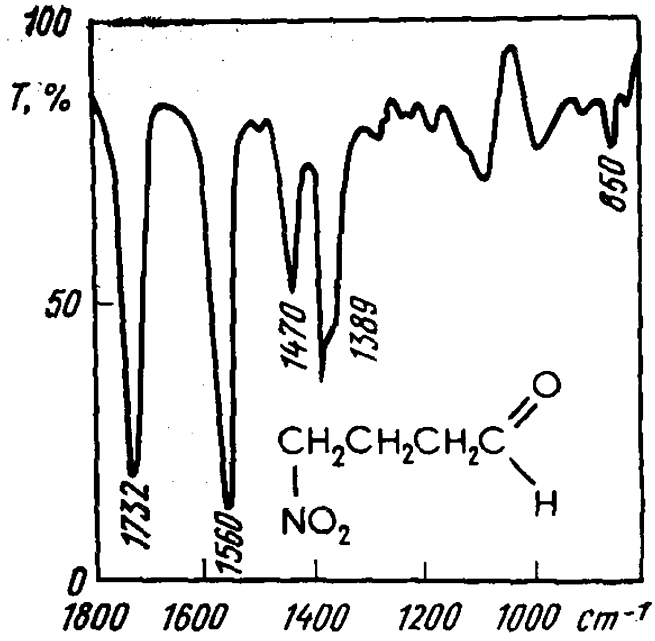
Problem 1. Assign the fundamental absorption bands of the IR spectrum given in Fig. 36 to the respective groups.

Answer. Aliphatic aldehyde—$\nu_{C=O}$ = 1732 cm^{-1}; NO_2—ν_{as} = 1560 cm^{-1} and ν_s = 1389 cm^{-1}; CH_2—δ = 1470 cm^{-1}; C—N—ν = 850 cm^{-1}.

Problem 2. Assign the fundamental bands of the spectrum given in Fig. 37 to the vibrations of respective groups.

* In solving the problems make use of the characteristic frequencies given in the Appendix.

Fig. 36.



Answer. High-intensity bands: ONO_2—$\nu_{as} = 1650$ cm^{-1}, $\nu_s = 1280$ cm^{-1}; NO_2—$\nu_{as} = 1565$ cm^{-1} and $\nu_s = 1385$ cm^{-1}. The bands at 875 and 850 cm^{-1} are assigned to the vibrations of the C—N bond.

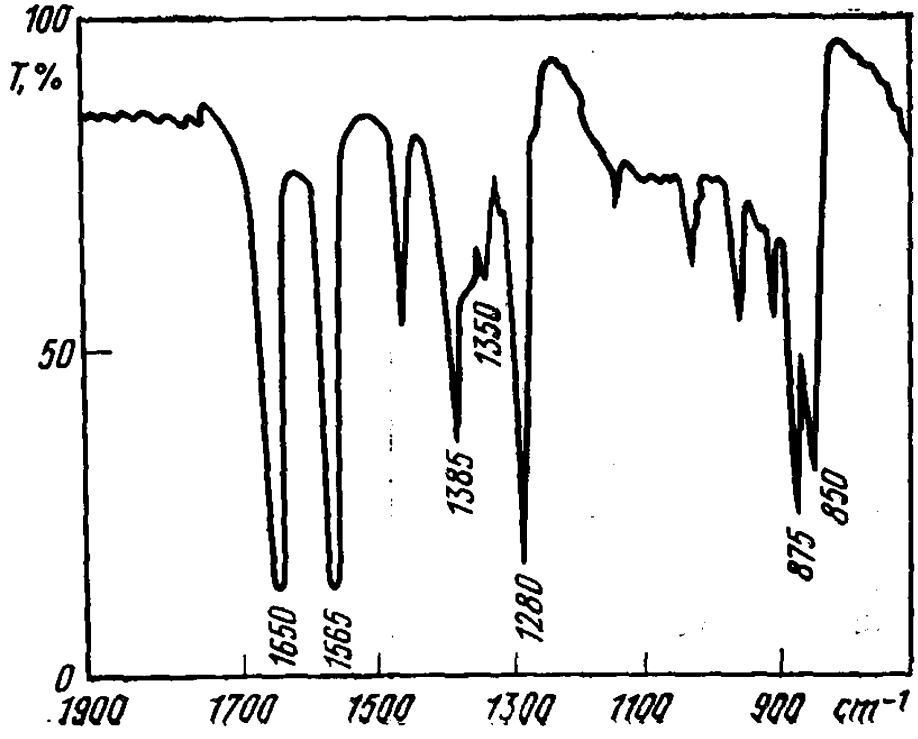


Fig. 37.

Problem 3. The IR spectrum of the compound with the empirical formula $C_5H_5SO_3$ is given in Fig. 38. Identify the groups in the compound.

Answer. The spectral data suggest the presence of the carbonyl, SO_2 or S=O groups. The high-intensity band with $\nu_{C=O} = 1722\ cm^{-1}$ is characteristic of ketone.

Assignment of bands to the groups S=O or SO_2 is not easy since the spectrum comprises both the high-intensity band at 1065 cm^{-1} characteristic of sulphoxides (1070-1030 cm^{-1}) and the bands characteristic of sulphones

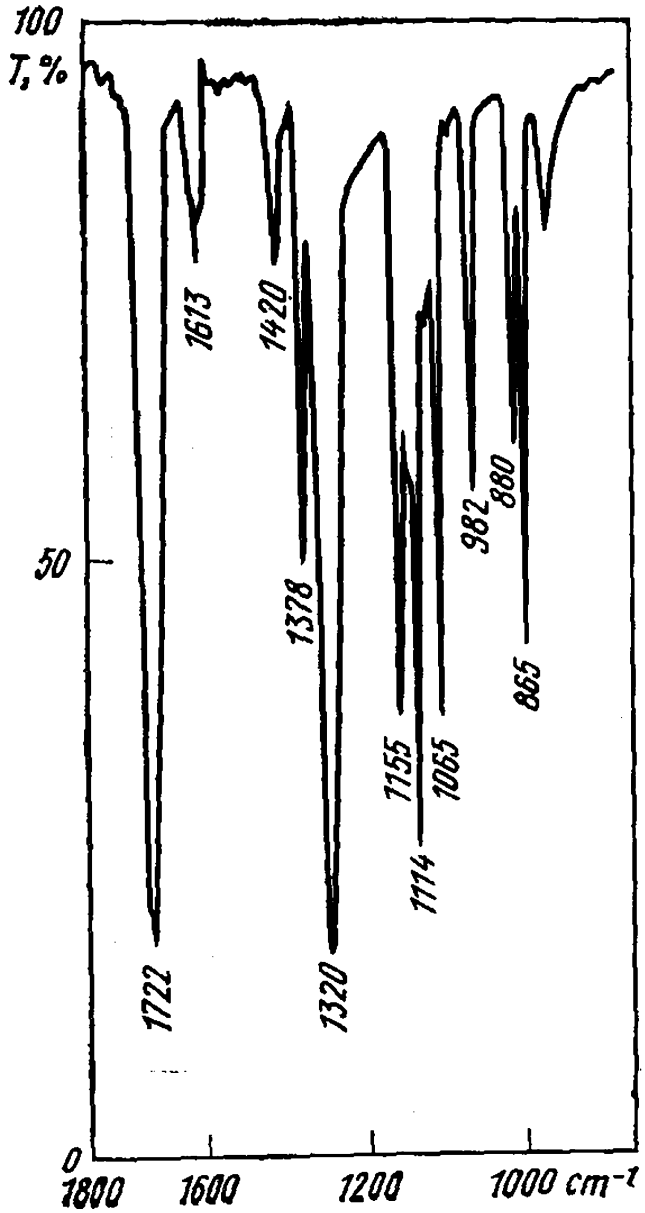
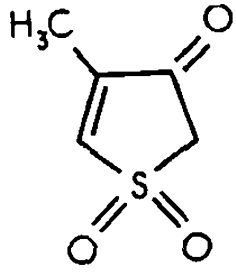


Fig. 38.

(ν_{as} = 1350-1300 cm^{-1}, ν_s = 1160-1120 cm^{-1}). However, the symmetric stretching bands of SO_2 are known to have often a complex structure with satellites on both sides of the main peak. Therefore, the bands at 1320 (ν_{as}), 1115, 1114 and 1065 cm^{-1} (ν_s) should be assigned to the sulpho group. The band at 1613 cm^{-1} is due to vibration of the double bond in the ring:



Problem 4. The IR spectrum of the compound with the empirical formula $C_7H_{13}N_3O_7$ is given in Fig. 39. Determine which groups of the compound contain oxygen and nitrogen atoms.

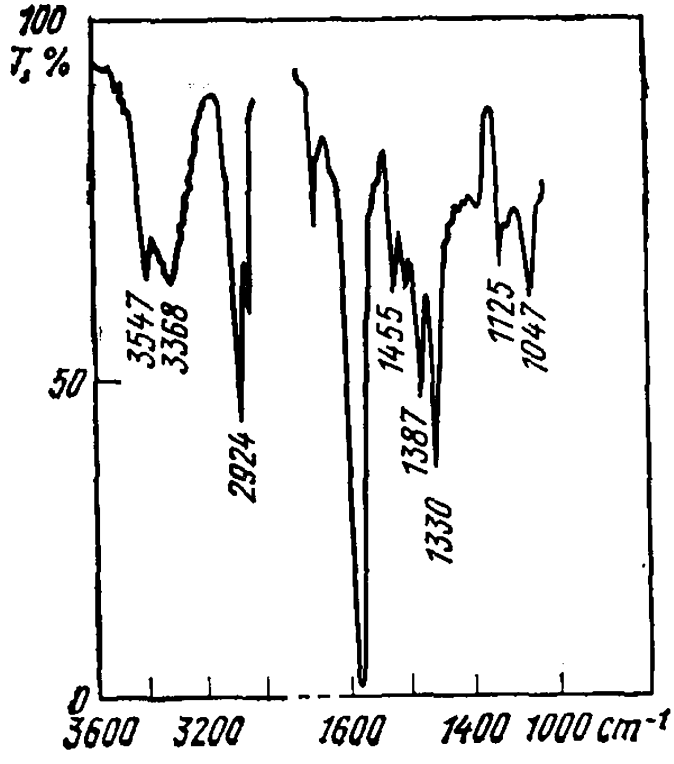


Fig. 39.

Answer. The high-intensity band at $\nu_{as} = 1590$ cm^{-1} and the band at $\nu_s = 1330$ cm^{-1} can be assigned to the trinitromethyl group. This group is characterized by a large frequency difference $\Delta\nu = \nu_{as} - \nu_s = 260$ cm^{-1}. In the 3500-3360 cm^{-1} range the wide band can be identified as ν_{OH}, the band at 2924 cm^{-1} as ν_{CH_2} and ν_{CH}, the band at 1455 cm^{-1} as δ_{as} for the group CH_3, the band at 1387 cm^{-1} as δ_s for the group CH_3 and the bands at 1125 and 1047 cm^{-1} as δ_{C-O-H}. Hence, the compound has the structure

$$CH_3(CH_2)_2CH_2-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_2-C(NO_2)_3$$

1,1,1-trinitro-3-heptanol

Problem 5. Assign the bands of the IR spectrum given in Fig. 40.

Answer. The character of the bands in the 3500-3000 cm^{-1} range indicates association of the NH group. The band at 1640 cm^{-1} should be assigned to the CO group. The frequency $\nu_{C=O}$ is low owing to the involvement of the

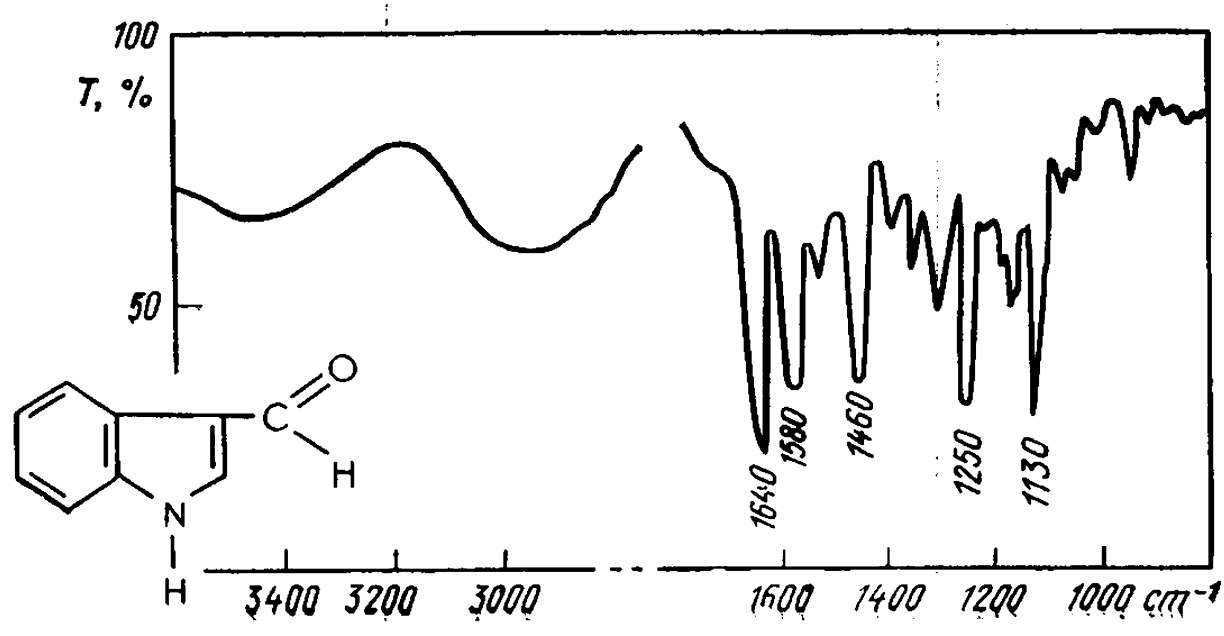


Fig. 40.

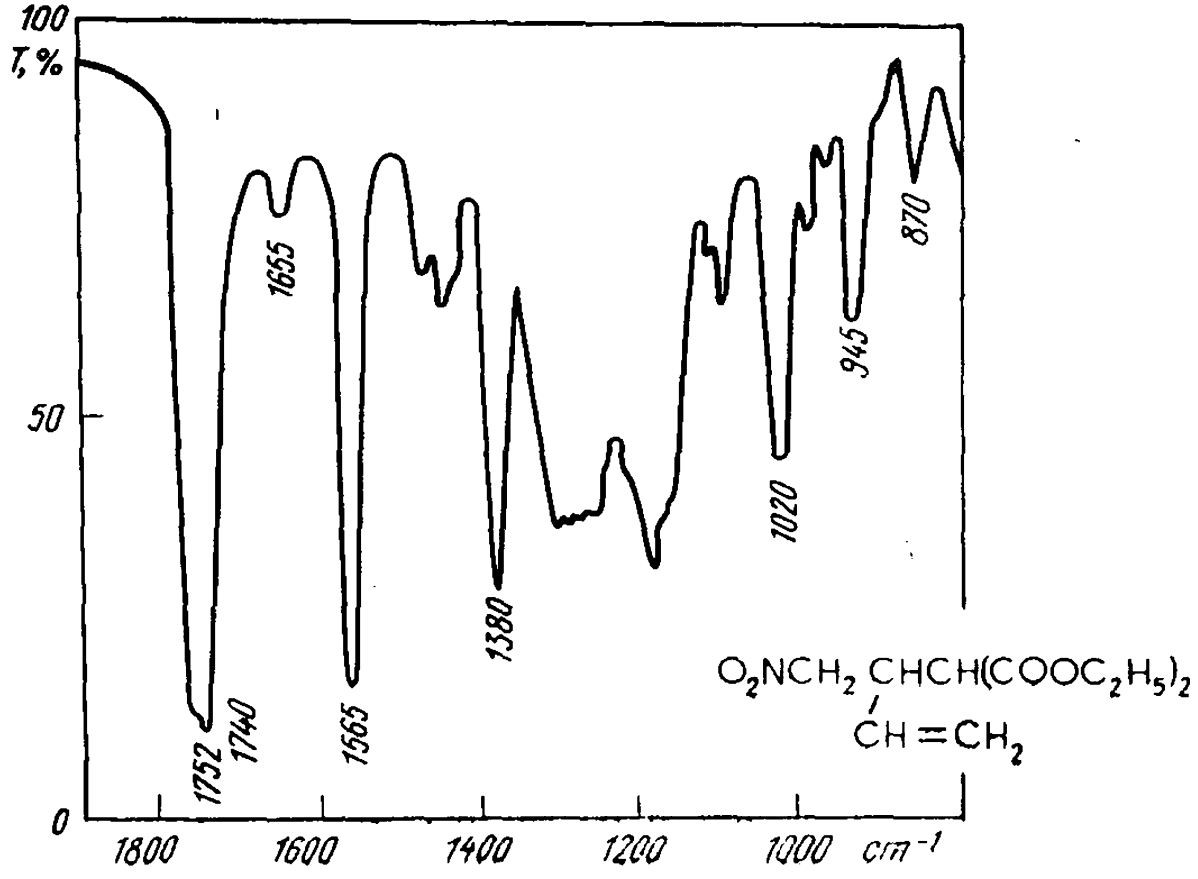


Fig. 41.

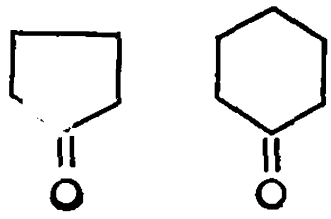
carbonyl group in hydrogen bonding and to conjugation. The band at 1580 cm^{-1} can be assigned both to vibrations of the ring and to vibrations of the C=N bond. The bands at 1460 and 1130 cm^{-1} are due to vibrations of the ring.

Problem 6. Correlate the IR absorption spectrum, given in Fig. 41, with the structure of the compound.

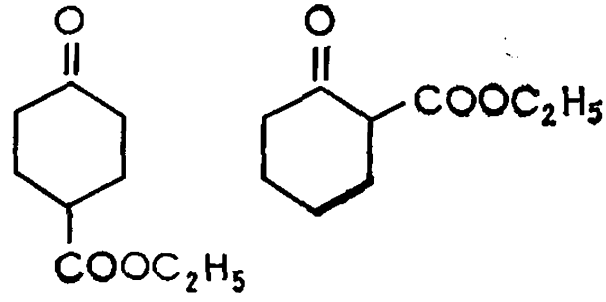
Answer. The bands at 1752 and 1740 cm^{-1} are due to the ester unit. The band at 1655 cm^{-1} should be assigned to the vibration of the double bond. The bands with ν_{as} = = 1565 cm^{-1} and ν_s = 1380 cm^{-1} are characteristic of the nitro group. The bands at 1200 and 1020 cm^{-1} are due to vibration of the C=O bond and the bands at 945 and 870 cm^{-1} are due to vibration of the C–N bond.

Problem 7. Make use of the IR spectroscopy to distinguish between the members of the following pairs of compounds:

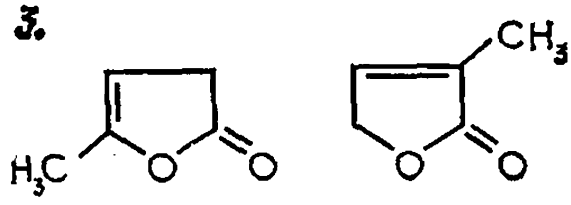
1.



2.

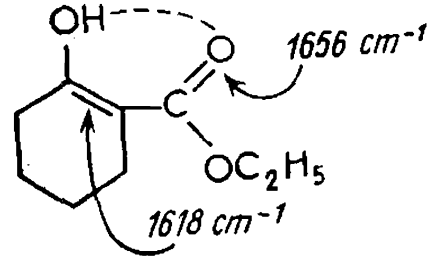


3.



Answer. 1. The absorption frequency $\nu_{C=O}$ of cyclopentanones (1745 cm^{-1}) is higher than that of cyclohexanes (1715 cm^{-1}) owing to stressing of the cycle.

2. The compound containing the ester group at the *para*-position should exhibit absorption bands of the carbonyl and ester groups ($\sim$1720 and $\sim$1740 cm^{-1}). The compound containing the ester group at the *ortho*-position may be a mixture of the keto-ester and enol ester. Hence, such a compound may have four absorption bands at about 1740, 1720, 1656 and 1618 cm^{-1}:



3. In saturated γ-lactones the absorption band for the C=O group is typically found at 1770 cm^{-1}. When the C=O group is conjugated with a double bond its band is shifted to 1750 cm^{-1}.

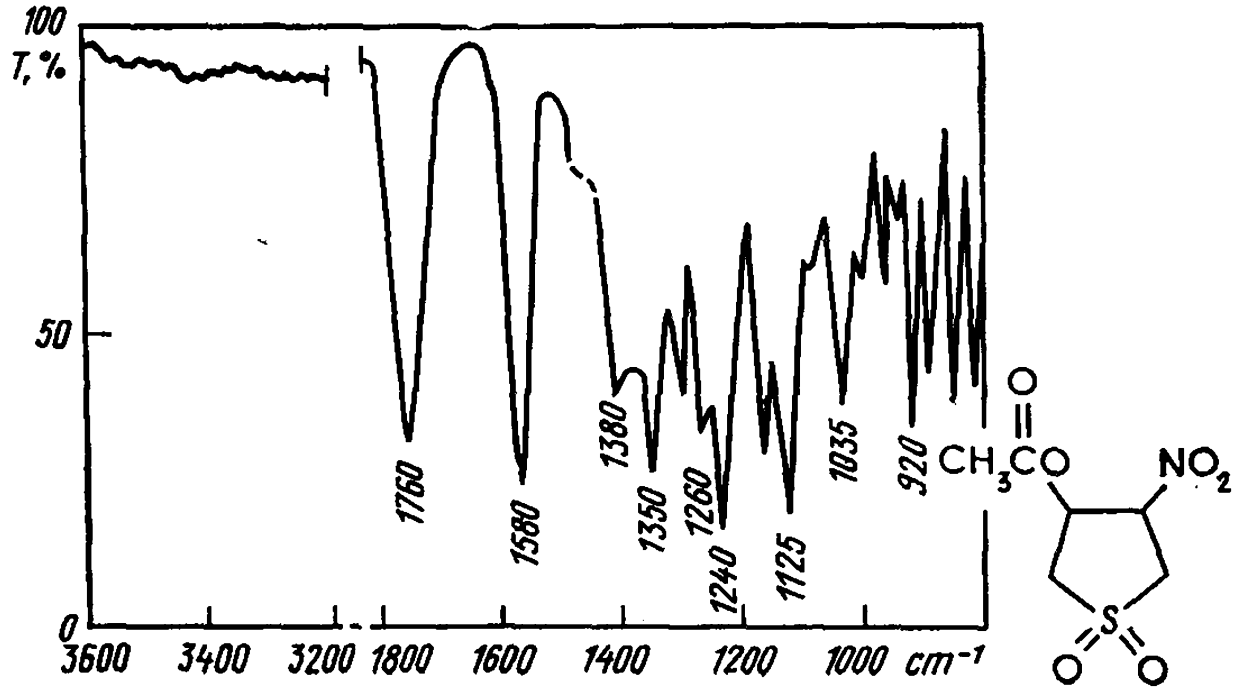


Fig. 42.

Problem 8. Correlate the fundamental bands in the IR spectrum given in Fig. 42 with the structure of the compound.

Answer. The band at 1760 cm^{-1} is assigned to the carbonyl group. The unconjugated nitro group has characteristic bands at 1580 and 1380 cm^{-1}. The bands at 1350 (ν_{as}) and 1125 cm^{-1} (ν_s) should be assigned to the sulpho group. The bands at 1240 and 1260 cm^{-1} may be due to vibration involving the C—O bond.

Problem 9. The reaction between 1,4-dinitro-1,3-cyclohexadiene (Fig. 43) with styrene gave rise to a reaction product whose spectrum is shown in Fig. 44. Compare the spectra of the initial compound and the product.

Answer. A comparison of the spectra shows that in the spectrum of the reaction product the absorption bands of the nitro group (ν_{as} and ν_s) are shifted to higher frequencies owing to the fact that the nitro group is not conjugated with the π-electrons of the double bond. This is an example

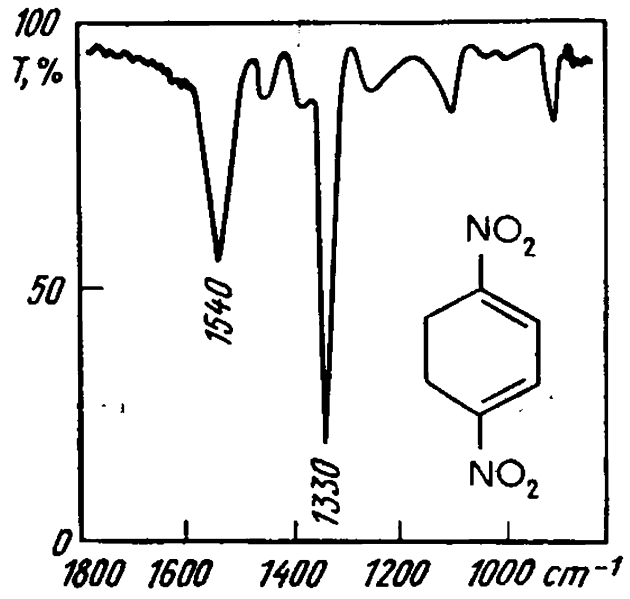


Fig. 43.

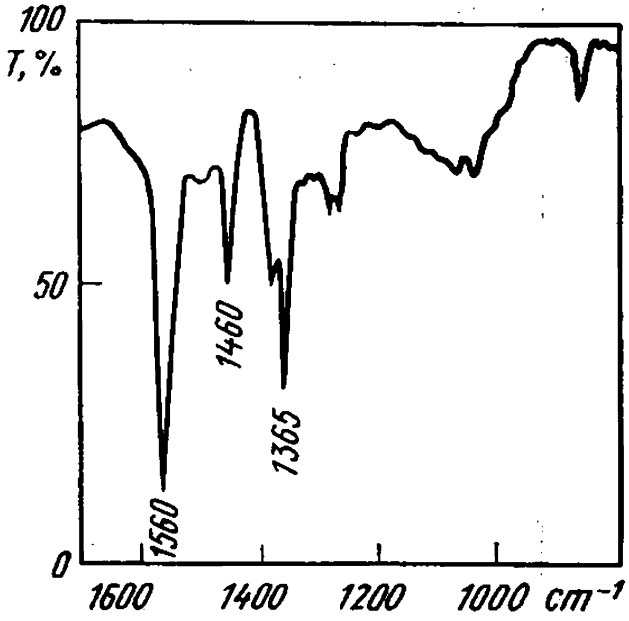
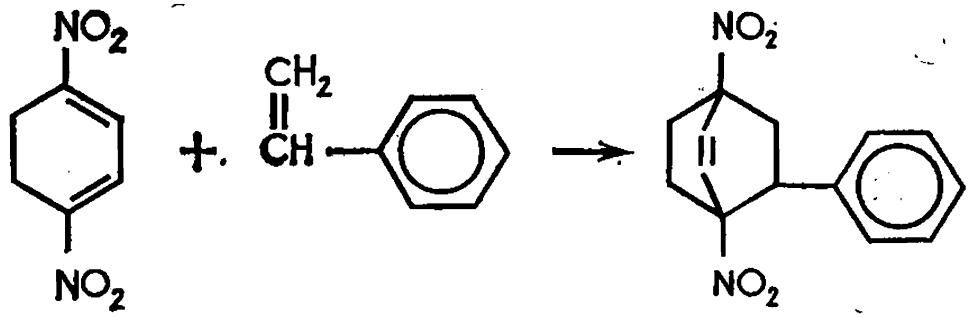


Fig. 44.

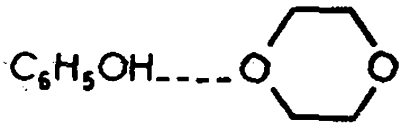
of the Diels-Alder reaction of diene synthesis with the "reversed" electronic character:



Problem 10. The IR spectrum of *cis*-1,2-cyclopentandiol contains the absorption band of the OH group at a lower frequency than that of the free OH group, and the band does not disappear even at high dilutions. No such band is found in the spectrum of *trans*-1,2-cyclopentandiol. Explain these observations.

Answer. The *cis*-isomer has the intramolecular hydrogen bonding.

Problem 11. Phenol forms a hydrogen bond with dioxane:



Predict the changes in the strength of this hydrogen bond for the phenol molecules with the following substituents: *p*-CH_3, *m*-Cl, *p*-Cl, *p*-NO_2, *m*-CH_3O, *p*-CH_3O.

Answer. The strength of the intermolecular hydrogen bond between dioxane and various substituted phenols depends on the degree of protonization of the hydrogen atom in the hydroxyl group. The interaction with the oxygen atom of dioxane becomes stronger with increasing acidity of phenol. The hydrogen bond between dioxane and substituted phenols becomes weaker in the following order of substituents: *p*-NO_2, *m*-Cl, *p*-Cl, *m*-OCH_3, H, *p*-CH_3, *p*-OCH_3. This conclusion is confirmed by the IR spectra of phenol solutions in dioxane. Given below are the shifts of the hydroxyl band in dioxane solutions, with respect to the hydroxyl band in the phenol solution in carbon tetrachloride:

phenol—272 cm^{-1},
p-cresol—270 cm^{-1},
p-chlorophenol—299 cm^{-1},
m-chlorophenol—314 cm^{-1}.

Problem 12. Predict the possibility of formation of the intramolecular hydrogen bond and the relative strength of this bond for the compounds described in Table 14 using the IR spectral data given therein.

Answer. To predict formation of the hydrogen bond in the cyclic diols and its relative strength one should take into account the spatial arrangement of the hydroxyl groups in various conformations. Highly dilute solutions in carbon tetrachloride are typically used to rule out the formation of the intermolecular hydrogen bonds. The diols forming

TABLE 14

ABSORPTION BANDS OF THE HYDROXYL GROUPS IN THE IR SPECTRA OF CYCLOALKANDIOLS

Compound	ν_{free} (cm^{-1})	ν_{bound} (cm^{-1})	$\Delta\nu$ (cm^{-1})
cis-1,2-Cyclopentandiol	3633	3572	61
trans-1,2-Cyclopentandiol	3620	—	—
cis-1,2-Cyclohexandiol	3626	3587	39
trans-1,2-Cyclohexandiol	3634	3602	32
cis-1,3-Cyclohexandiol	3616	3544	72
trans-1,3-Cyclohexandiol	3620	—	—
cis-1,4-Cyclohexandiol	3629	—	—

intramolecular hydrogen bonds exhibit two absorption bands associated with vibrations of the free hydroxyl and the hydroxyl involved in hydrogen bonding. The hydrogen bond is the stronger the larger the difference between the peaks of the stretching bands of the free and bound hydroxyl groups.

Problem 13. Assign the fundamental bands of the IR spectrum given in Fig. 45 to the appropriate groups of the compound.

Answer. The bands at 3390, 3180 and 1620 cm^{-1} may ndicate the presence of the primary amino group. The

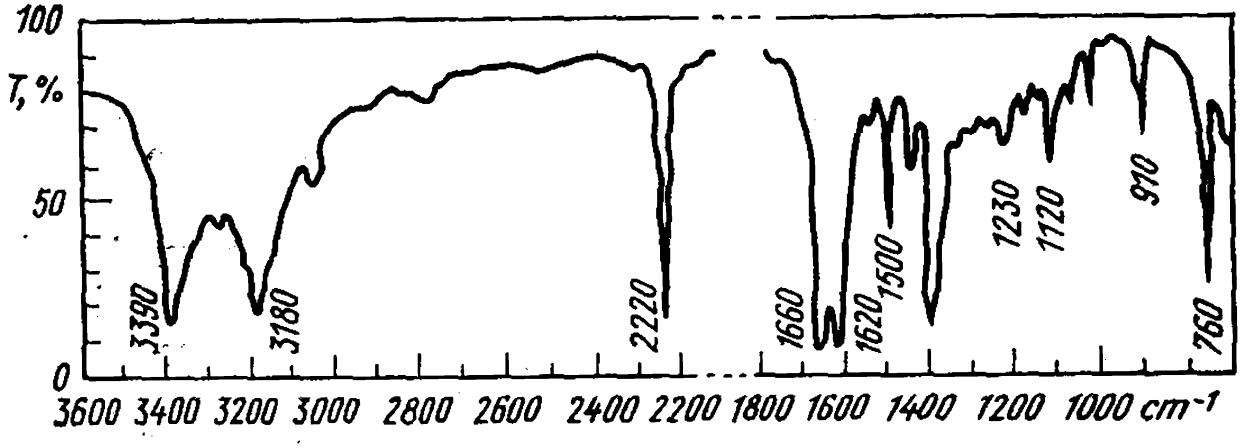
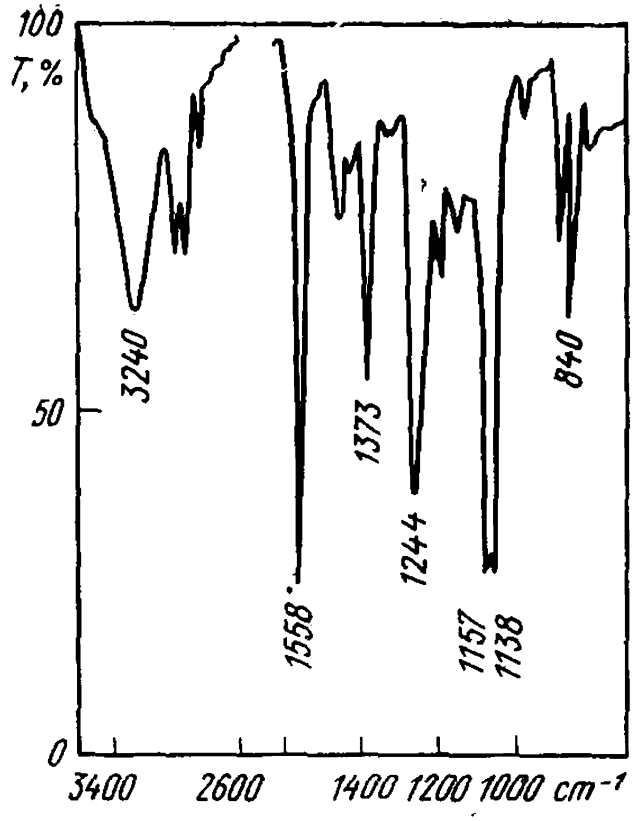
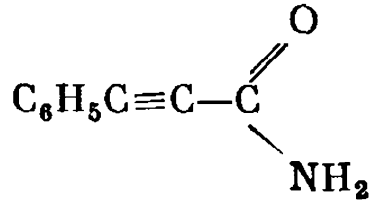


Fig. 45.

Fig. 46.



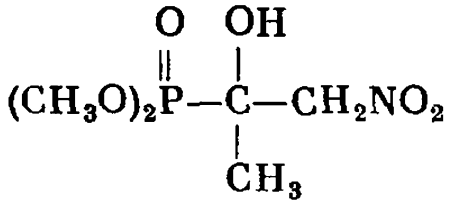
high-intensity band at 2220 cm^{-1} indicates a conjugated triple bond. The bands at 3050, 1500, 1450 and 760 cm^{-1} are assigned to vibrations of the aromatic ring, and the band at 1660 cm^{-1}, to the carbonyl group. Hence, the structure of the compound is



Problem 14. Identify the oxygen-, nitrogen- and phosphorus-containing groups in the compound whose spectrum is shown in Fig. 46.

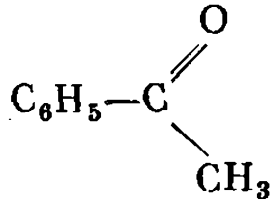
Answer. The lack of an absorption band in the 1800-1600 cm^{-1} range indicates the absence of the carbonyl group. The high-intensity absorption bands of complex structure in the 3240-3000 cm^{-1} range are due to the hydroxyl group. The high-intensity bands at 1558 and 1373 cm^{-1}

are characteristic of the (unconjugated) nitro group. The band at 1244 cm^{-1} is assigned to the vibration of the P=O bond, and the bands at 1157 and 1138 cm^{-1} are assigned to the vibration δ_{C-O}. The compound has the structure



Problem 15. Identify the structure of the compound C_8H_8O whose spectrum contains the following absorption bands: 1680 (strong), 1600 (medium), 1580 (medium), 1450 (medium), 1430 (strong), 1360 (strong), 1265 (strong), 755 (strong) and 690 (strong) cm^{-1}.

Answer. The empirical formula suggests the following structure for the compound:

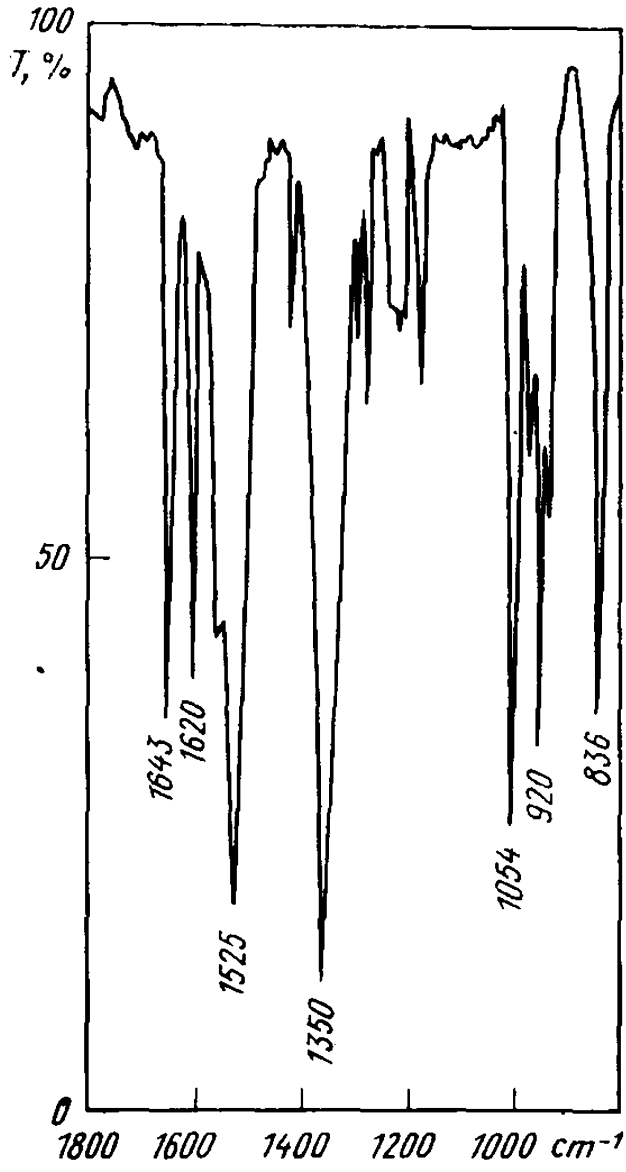


The IR spectral bands agree with this structure. The monosubstituted benzene ring has the characteristic bands at 1600, 1580, 1450, 750 and 690 cm^{-1}, the characteristic bands for the aromatic ketone are at 1680 and 1275 cm^{-1}, and those for the methyl group are at 1430 and 1360 cm^{-1}.

Problem 16. Assign the fundamental bands of the IR spectrum given in Fig. 47 to the appropriate groups of the compound.

Answer. The bands at 1643 and 1620 cm^{-1} are characteristic of the diene structure. The fairly high intensity of these bands is attributed to conjugation of the nitro groups with the π-electrons of the double bonds. The bands at 1525 and 1350 cm^{-1} may be assigned to the conjugated nitro group. Hence, the compound may have the structure $CH_2=CH-CH=CHNO_2$.

Fig. 47.



Problem 17. Identify the main structural elements of a compound from its IR spectrum given in Fig. 48.

Answer. The high-intensity band at 1708 cm^{-1} is due to vibration of the carbonyl group. The low frequency of this band results from the effect of the phosphorus atom. The band at 1261 cm^{-1} should be assigned to vibration of the P=O bond. The bands at 2987, 2960, 1420 and 1350 cm^{-1} are produced by the stretching and deformation vibrations of the CH_3 groups.

Problem 18. Compare the spectra of the compounds shown in Figs. 49, 50 and 51 and make a qualitative evaluation of

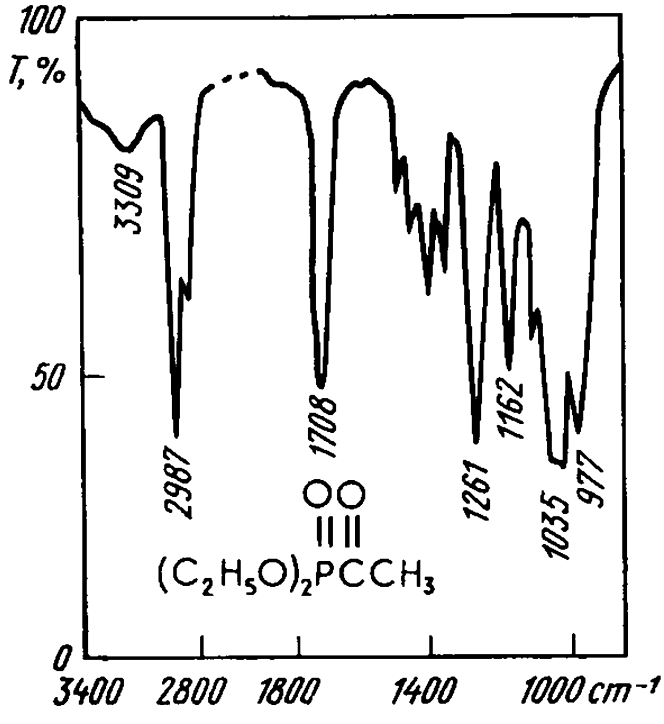


Fig. 48.

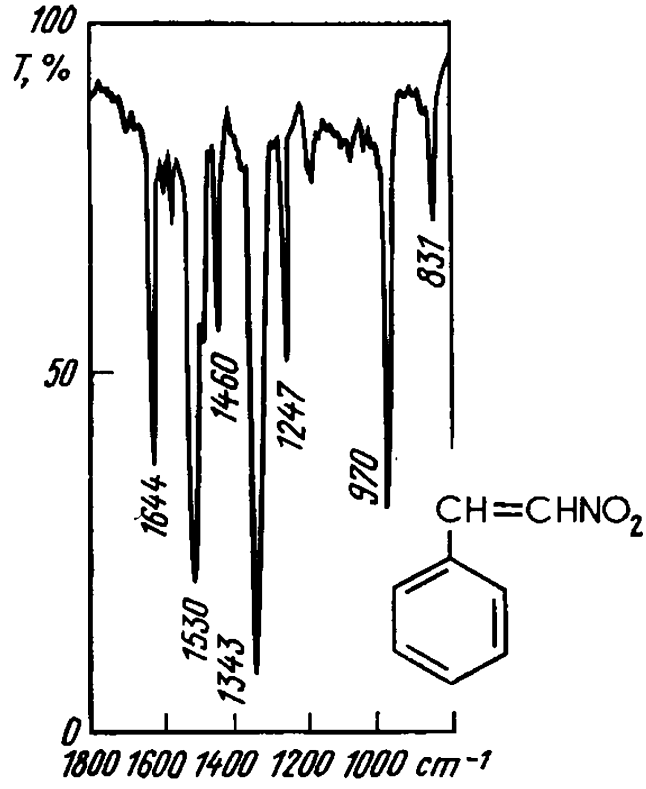


Fig. 49.

the effect of the substituents at the α-position with respect to the nitro group, on the positions of the absorption bands of the nitro group and of the double bond.

Answer. Let us tabulate the fundamental spectral data for the compounds under consideration (Table 15).

TABLE 15

Substituent	NO_2		$\Delta\nu$ (cm^{-1})	$\nu_{C=C}$ (cm^{-1})
	ν_{as} (cm^{-1})	ν_s (cm^{-1})		
H	1530 (strong)	1343 (strong)	187	1644 (medium)
CH_3	1528 (strong)	1318 (strong)	210	1655 (medium)
Br	1540 (strong)	1312 (strong)	228	—

The spectral data of Table 15 show that the substituents at the α-position (CH_3, Br) with respect to the nitro group affect the frequencies of the stretching vibrations (ν_{as} and ν_s) of the nitro group. Substitution with the bulky methyl group and the bromine atom results in a marked increase in the difference between the frequencies of the nitro group absorption bands. The electronegative substituents typically shift the antisymmetric stretching band of the nitro group to higher frequencies while the frequency ν_s decreases by about 40 cm^{-1}. Similar effects are found in the spectra of other nitro compounds. If the α-substituent is the CH_3 group, the frequency $\nu_{C=C}$ of vibration of the double bond increases owing to weaker conjugation of the nitro group with the π-electrons of the double bond (the band intensity decreases).

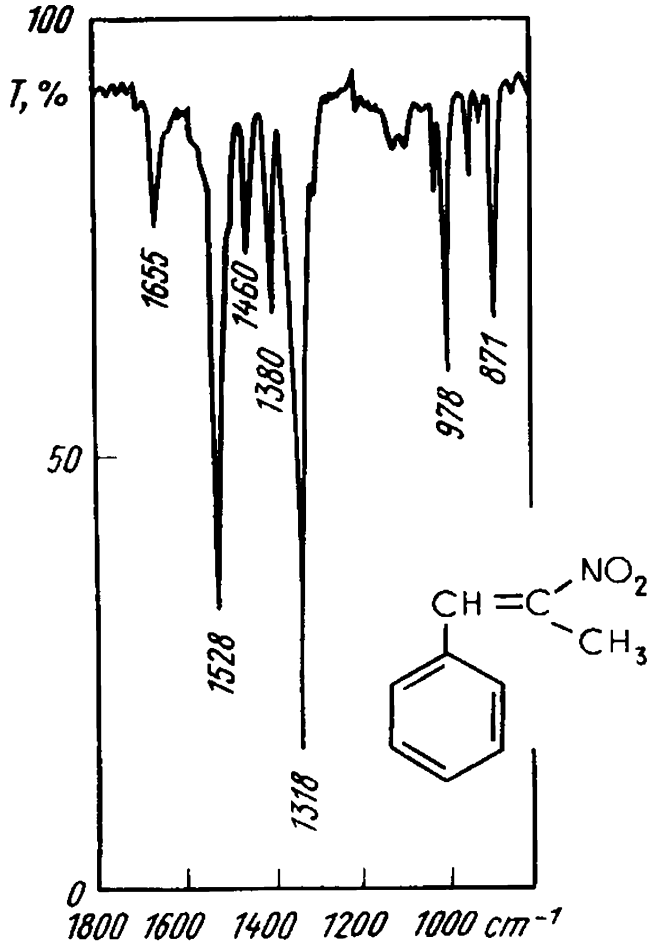


Fig. 50.

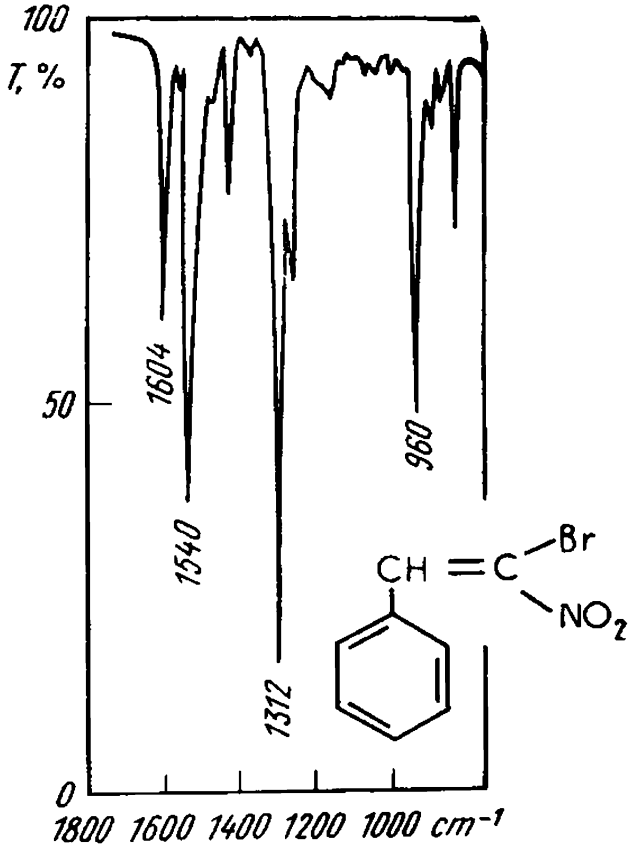


Fig. 51.

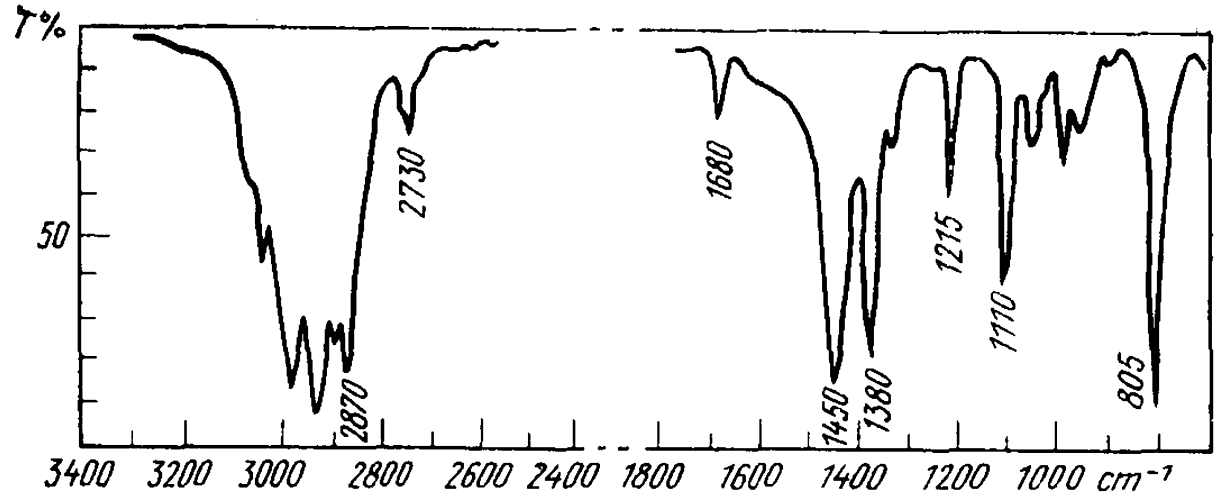


Fig. 52.

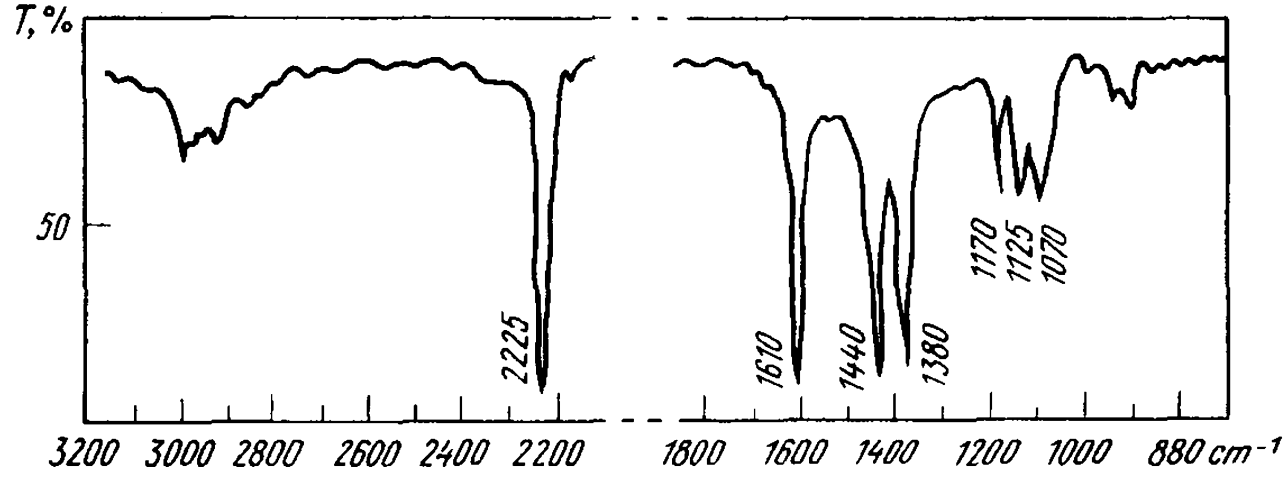


Fig. 53.

The other bands are assigned to vibrations of the benzene ring (~1600 and 1460 cm^{-1}), of the methyl group (δ_{CH_3} = = 1380 cm^{-1}) and of the bonds C—H and C—N (~970, 870 and 830 cm^{-1}).

Problem 19. Compare the spectra shown in Figs. 52 and 53 and explain the high intensity of the absorption band of the CN group in the compound 2:

1. H_3C, H_3C, $C=CH-CH_3$

2. H_3C, H_3C, $C\equiv N$, $C\equiv N$, $C=C$

Answer. The spectra of these two compounds have the following common features: the *gem*-dimethyl groups have characteristic bands at 3000-2650 cm^{-1} (ν_{as} and ν_s), 1460 and 1380 cm^{-1} (δ_{as} and δ_s) and 1250-1150 cm^{-1} (skeletal vibrations).

The band of the double bond is found at 1680 cm^{-1} for the compound 1 and at 1610 cm^{-1} for the compound 2. Significant differences are found in the intensities of the absorption bands. For the compound 2 the band of the tetrasubstituted double bond is at lower frequencies and has a much higher intensity than that of the trisubstituted one. This effect is due to a higher polarization of the double bond under the influence of the electron-acceptor nitrile groups. The high intensity of the absorption band at 2225 cm^{-1} can be attributed to the presence of two conjugated nitrile groups.

TABLE 16

Substituent	ν_{NO_2} (cm^{-1})		$A \cdot 10^{-4}$ (red. units)		$\nu_{C=C}$ (cm^{-1})	$A \cdot 10^{-4}$ (red. units)
	as	s	as	s		
H	1540	1350	2.1	1.02	1640	0.1
CH_3	1537	1342	1.4	1.2	1657	0.2
C_2H_5	1535	1355	1.8	1.8	1650	0.34
$CH_2=CH$	1525	1350	—	2.5	1643 1610	—
C_6H_5	1530	1333	1.8	3.1	1640	0.6
$H_3C-C_6H_4$	1514	1340	—	3.6	1635	1.05
$C_6H_5-C_6H_4$	1515	1336	—	4.2	1638	—
$C_6H_5CH=CH$	1520	1339	2.03	5.2	1634	—

Problem 20. Table 16 presents spectroscopic data (frequency and integral intensity) for a series of substituted nitroethylenes ($RCH=CHNO_2$). Using these data estimate the degree of conjugation of the nitro group with the π-electrons of the double bond.

Answer. The degree of conjugation can be determined from the integral intensity A_s of the symmetric stretching band of the nitro group. The integral intensity varies regularly in a wide range from 1 red. unit for nitroethylene to 5.2 red. units for 1-nitro-4-phenyl-1,3-butadiene. The integral intensity of the absorption band of the double bond ($A_{C=C}$) varies in accordance with variation of A_s.

Hence, it can be concluded that the highest degree of conjugation of the nitro group with the π-electrons is found in 1-nitro-4-phenyl-1,3-butadiene. It would be difficult to make this conclusion proceeding only from the band frequency data.

LABORATORY EXERCISES

Exercise 1. IR Spectroscopic Instruments and Techniques

The following IR double-beam spectrophotometers are widely used in the USSR: ИКС-14, ИКС-22, UR-10 and UR-20 (manufactured in GDR). The instrument ИКС-14 (with changeable prisms) records the IR absorption spectra in the 13 300-400 cm^{-1} range. The instrument ИКС-22 with a sodium chloride prism operates in the 5000-650 cm^{-1} range. Other spectrophotometers have prisms of KBr, LiF, CsI and operate in various spectral ranges. The 5000-400 cm^{-1} range is generally sufficient for structural studies of organic compounds. The instruments ИКС-14 and ИКС-22 have similar designs.

These instruments can operate both in the single-beam and double-beam modes. The spectrum is recorded with a pen on a chart paper. An infrared spectrophotometer comprises a monochromator, a two-beam radiation source and a recorder mounted on the same frame. The optical null concept is used for the double-beam operation of the

spectrophotometer. The radiation of the source is split with mirrors into two beams one of which passes through the sample cell and the other through the photometric wedge and the reference cell. Both beams get to the chopper which alternately transmits the reference beam and the sample beam to the monochromator. If there is no absorption in the sample beam both beams deliver the same energy to the detector (bolometer) producing the null signal. If a part of the energy of the sample beam is absorbed, the intensities of the beams are different and the detector produces a signal varying with the frequency of chopping. This signal is amplified, converted and fed to the servomotor which drives the wedge to make the null signal difference between the sample beam and the reference beam. The wedge is mechanically coupled with the recording pen which indicates on the chart paper the position of the wedge and, thus, the absorption of energy by the sample. The radiation source is a silit rod—a Globar—with the luminance temperature of 1300-1400° C.

For the wavelength calibration of spectrophotometers it is useful to record the absorption spectra of the compounds whose peak wave numbers are sufficiently well known. The spectra of these compounds should contain a sufficient number of narrow bands. This requirement is satisfied by the vibrational-rotational bands of some simple molecules (HCl, HBr, CO, H_2O, NH_3) where peak positions are known to 0.01 cm^{-1}. Certain liquids and solid films can also be used in some cases.

The IR spectrophotometers with lithium fluoride or sodium chloride prisms are typically calibrated with a 25 μm polystyrene film which has characteristic absorption bands at 2850, 1603 and 906 cm^{-1}. One of the above bands is, typically, used for calibration in combination with the bands of gaseous ammonia in the 3500-3100 and 1250-700 cm^{-1} ranges (100 mm layer, pressure 200 mm Hg), the bands of the gaseous hydrogen chloride in the 3100-2600 cm^{-1}

range, the bands of hydrogen bromide in the 2600-2400 cm^{-1} range and the bands of carbon monoxide CO in the 2200-200 cm^{-1} range. The instruments are also calibrated with liquid benzene and chloroform in 1-cm cells.

To select an IR spectroscopic technique suitable for a given sample the following factors should be taken into account: the goals pursued in the analysis, the state of aggregation of the sample, and its solubility in the solvent being used. The IR spectra can be recorded for the samples of any phase—liquid, solid, and gaseous. The most widely used procedure is to record the IR spectra of solutions since it enables us to carry out various qualitative and quantitative studies (of the reaction kinetics, inter- and intramolecular interactions, etc.).

The solvent can be any organic solvent which is transparent in a given spectral region. The most widely used solvents in IR spectroscopy are carbon tetrachloride, chloroform and carbon disulphide. These solvents are used when the sample layer is 0.05-10 mm thick.

The solvent used in IR spectroscopy should satisfy the following requirements: it should be free of water, the solubility of the analyzed compound should be high, and it should not have strong absorption bands in the spectral range under study. Another factor limiting the range of applicable solvents is the fact that the IR cells have windows made, typically, of halides of alkaline metals (NaCl, KBr). For instance, water cannot be used as it can dissolve the cell window.

IR spectroscopic analysis of a solid sample makes possible qualitative analysis of the spectrum of the compound over the entire frequency range. The IR spectrum of a solid sample is not identical with the IR spectrum of the same compound in solution since the first spectrum reflects the intermolecular interactions in the unit cell of the crystalline lattice. The spectra of different crystalline modifications of the same compound can prove to be not identical. Solid

samples are typically made in the form of pressed pellets containing a halide of an alkaline metal, mostly, potassium bromide.

Special sealed gas cells are used for recording the spectra of gases.

Operational procedure:

(1) When an ИКС-22 spectrophotometer is used* (in the double-beam operational mode) switch on the power supply of the thermostat and warm up the system for 1 hour to the steady-state temperature regime.

(2) Activate the amplifier, the water cooling system and the Globar and adjust the light sector to 15-20° on the indicator screen.

(3) Select the spectral range for recording, set the scale factor and the scanning speed, insert the appropriate strip chart and adjust the "wave number" control to it.

(4) Switch on the servomotor and the chopper motor, open both channels and select the gain at which a short-time shutting of the sample channel results in a rapid enough motion of the pen along the ordinate.

(5) Align the pen to the chart paper and set it to the 100% transmittance line by adjusting the photometric wedge.

(6) Insert the sample cell and the reference cell, switch on the scan motor and record the spectrum in the selected spectral range.

Exercise 2. Recording of the Absorption Spectra of Solutions

Operational procedure:

(1) Adjust the instrument and record the spectrum of the polystyrene film** (compare the recorded spectrum with the spectrum given in Fig. 54).

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* When another spectrophotometer model is used the operating instructions should be consulted.

** In all cases calibration can be carried out on the absorption band of polystyrene (1603 cm^{-1}) used as a standard (reference) material.

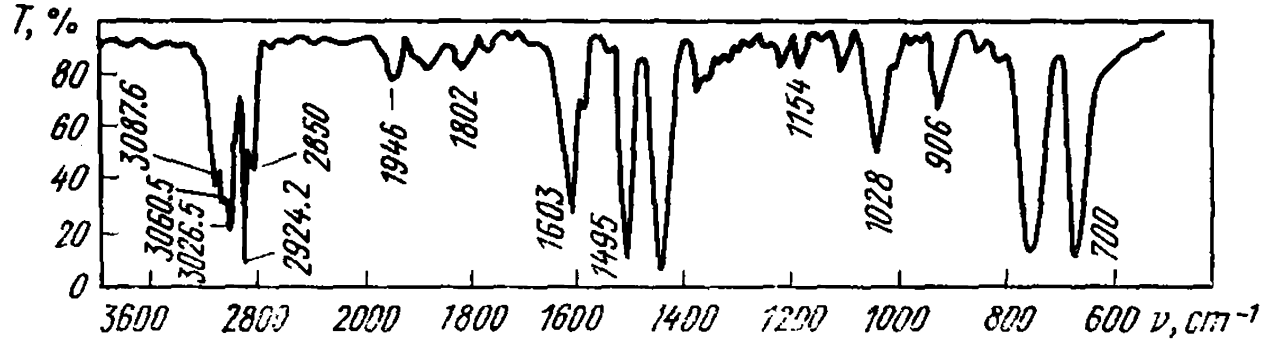


Fig. 54.
The absorption spectrum of polystyrene film.

(2) Prepare a few samples (for instance, nitrostyrene, acetophenone, or any other compounds with a polar group). Dissolve a weighed portion (about 100 mg) of the compound in 2.5 ml of chloroform.

(3) Assemble two identical cells and fill one with the solvent and another with the solution.

(4) Mount the cells in the respective channels of the spectrophotometer and estimate the optical density of the solution (the highest peak of the spectrum must not be higher than 20%-transmittance).

(5) If the optical density of the solution does not provide for the optimum conditions of recording, increase or decrease the layer thickness and repeat the estimating procedure.

(6) Record the spectrum in the 4000-650 cm^{-1} range.

(7) Identify the spectral regions containing a larger number of absorption bands and assign the bands to vibrations of groups and bonds using the table of characteristic frequencies given in the Appendix.

(8) Mount the cell with the solvent in the sample channel and record the spectrum of chloroform (with reference to air).

(9) Compare the recorded spectra.

Exercise 3. Group Structural Analysis of Organic Compounds

For the compounds containing the multiple bonds $\rangle C{=}C\langle$, $\rangle C{=}O$, $-C{\equiv}C-$, $-C{\equiv}N$ their IR spectra are analyzed to determine the positions of these bonds in the molecule and to estimate the effects of substituents.

Operational procedure:

(1) Using the tables of characteristic frequencies determine the range of stretching vibrations of the multiple bonds and the ranges of stretching and deformation vibrations of the C—H bond adjacent to the multiple bond.

(2) Prepare 5 cm^3 samples of 0.05 *M* solutions of styrene, phenylacetylene, acetone, acetaldehyde or other compounds in chloroform.

(3) Fill the sample cell with solution and the reference cell with the solvent. The layer thickness should be such that the peaks of the fundamental absorption bands vary from 40 to 80% absorbance (about 40 mg of the compound per 1 ml of the solvent for the layer thickness $l = 0.1$ mm).

(4) Record the spectra and analyze them.

Exercise 4. Analysis of a Mixture of Xylene Isomers

The IR spectra are used here to determine the concentrations of components in the mixture of *o*-, *m*- and *p*-xylene dissolved in cyclohexane.

Operational procedure:

(1) Record the absorption spectra of each isomer in cyclohexane in the 2000-600 cm^{-1} range. Assign the absorption bands to the appropriate vibrations whenever possible, and determine the common features of the three spectra and the differences between them. It should be noted that the positions and the relative intensities of the bands associated with the stretching vibrations of the double bond (the

benzene ring) at 1600, 1580, 1500 and 1450 cm^{-1} differ in these spectra. However, though these bands are influenced, to some extent, by the type of substitution, they yield little information on the structure of the compounds. For each type of substitution there is absorption in the 800-600 cm^{-1} range. The 1,3-disubstituted benzene has been found to have two high-intensity absorption bands in the 810-750 and 710-690 cm^{-1} ranges (out-of-plane deformation vibrations of the C—H bond); the 1,4-disubstituted benzene has one very strong band at 800 cm^{-1}, and the 1,2-disubstituted benzene absorbs in the 770-735 cm^{-1} range. Analyze the spectra of these compounds in the 800-600 cm^{-1} range.

(2) Prepare a mixture of the isomers (in approximately equal amounts), record the spectrum of the mixture, and compare it with the spectra of individual isomers. Find the bands characteristic for isomers in the spectrum and select the absorption band for the analysis of each isomer.

(3) Prepare three standard solutions of xylenes in cyclohexane* with given concentrations. To do this, first prepare three mixtures of *o*-, *m*- and *p*-xylene with given concentrations, for instance:

Compound	Concentration in mixture (%)		
o-xylene	65	5	15
m-xylene	20	75	5
p-xylene	15	20	80

The total volume of each mixture can be 25-50 cm^3. Dissolve 1 cm^3 of each mixture in 20 cm^3 of cyclohexane.

(4) Record the spectra of the samples.

* Here cyclohexane is the most convenient solvent since it does not have its own absorption bands in the 800-600 cm^{-1} range.

(5) Determine the optical density for the analytical absorption bands ($D = \log T_0/T$) and plot the function $D = f(c)$ for each of the three analytical bands.

(6) Dissolve an unknown mixture of xylenes in cyclohexane (1 : 20) and record its spectrum.

(7) Using the above plots determine the concentrations of the xylene isomers in the unknown mixture.

Exercise 5. Recording of the IR Spectra of Solids

Various techniques are used for recording the IR spectra of solids which are insoluble in organic solvents. A widely used and highly practicable technique is to prepare a suspension (a paste) of the solid in oil. Typically, the paste is made with a mixture of liquid high-molecular paraffin hydrocarbons (the mineral oil). The mineral oil is transparent in a wide spectral range (5000-3100, 2700-1500 and 1300-700 cm^{-1}) and has absorption bands at 3030-2860 (C—H stretching vibrations), and 1460 and 1375 cm^{-1} (C—H deformation vibrations). Thus, if the paste is prepared with the mineral oil, absorption of the analyzed compound cannot be studied in these spectral ranges. The mineral oil can be replaced with hexachlorobutadiene which has no C—H bonds so that it is transparent in the 4000-2000 and 1500-1000 cm^{-1} ranges. Thus, the full spectrum of a solid can be recorded in suspensions in mineral oil and hexachlorobutadiene. This exercise can be carried out with various organic solids such as acetanilide, *p*-nitroacetanilide, benzoic acid, *m*-nitrobenzoic acid, etc.

Operational procedure:

(1) Prepare the suspension (carefully grind 50 mg of the analyzed compound in 5 drops of mineral oil).

(2) Apply a thin layer of the suspension on a window of a demountable cell, cover it with another window, mount it in a holder and insert it into the sample channel of the spectrophotometer.

(3) Apply a few drops of mineral oil between two cell windows, mount them in a holder and insert them into the reference channel.

(4) Record the spectrum of the compound in a wide spectral range.

(5) Insert the reference cell into the sample channel, and a holder with windows without oil into the reference channel, and record the spectrum of the oil.

(6) Identify the bands of the oil in the spectrum of the compound.

(7) Assign the absorption bands of the compound to vibrations of its groups using the table of characteristic frequencies (see Appendix) (NH, $C(=O)CH_3$, $C(=O)OH$, NO_2).

Another technique of the IR spectroscopy of solids is to prepare pressed pellets. A weighed portion of the analyzed compound is mixed with carefully dried potassium bromide in the 1 : 100 ratio. The mixture is ground in an agate mortar. The powder is compressed in a die at a pressure of 4-5 tons per 1 cm^2. The dies are evacuated to prevent formation of air bubbles in the pellet which should be transparent. A pellet made of the same amount of pure potassium bromide is used as the reference when recording the spectrum.

Exercise 6. Interpretation of the IR Spectra

An absorption band is assigned to the appropriate bond vibration by comparing the spectra of a large number of the compounds of a similar structure. The aim of the exercise is to determine the frequency of the stretching vibration of the single bond C—O (in the fragment X—C—O—Y).

Materials: diethyl ether, dibutyl ether, diisopropyl ether, anisole, ethyl alcohol, propyl alcohol, *m*-cresol, ethyl acetate, hexane, acetone.

Operational procedure:

(1) Record the spectra of the ethers, alcohols and esters using thin films of liquid compounds as samples (1-2 drops of the liquid between sodium chloride plates). Use as reference the plates of the same material.

(2) Record the spectrum of hexane or acetone under the same conditions and analyze the spectra. Find the similarities and differences between the spectra.

It should be borne in mind that the frequency of the stretching vibration of a single bond is always lower than the stretching frequency for the respective double bond and, even more so, the triple bond, and the differences between vibration frequencies of single bonds are always larger than of multiple bonds.

The C—O band should have a high intensity since there is a large difference between the electronegativities of carbon and oxygen and since the vibration should result in displacement of the charges, that is, in significant variation of the dipole moment of the bond. A comparison of the spectra of ethers with the spectrum of acetone or hexane shows that the latter lacks the C—O absorption band.

(3) Tabulate the results and find the value of the mean frequency ν_{C-O} and the range of its variation. Can this frequency be used for structural analysis?

The table below presents the frequencies of vibrations of the carbon-carbon, carbon-nitrogen and carbon-oxygen bonds.

Bond	Frequency (cm^{-1})	Bond	Frequency (cm^{-1})
C ≡ C	2120±20	C = N	1650±40
C = C	1650±30	C — N	1100±100
C — C	about 1000	C = O	1720±20
C ≡ N	2250±10	C — O	?

Exercise 7. Keto-enol Tautomerism

Materials: acetoacetic ether, acetyl acetone, malonic ester, carbon tetrachloride, hexane, ether, chloroform, dimethylsulphoxide.

Operational procedure:

(1) Prepare 5, 4, 3, 2 and 1% solutions of acetoacetic ether in carbon tetrachloride.

(2) Record the IR spectra of each solution in the 1800-1500 cm^{-1} range with reference to the pure solvent (in 0.1-1.0 mm cells).

(3) Identify the absorption bands of the keto- and enol forms.

(4) Calculate their relative intensities ($\varepsilon = D/cl$).

(5) Plot the intensity of each of the bands as a function of concentration (ε vs. c). The ratio of the slopes of the plots is equal to the ratio of the contents of both forms in dilute solutions of carbon tetrachloride.

(6) Evaluate the effect of the solvent. Select the concentration of the acetoacetic ether for which a good spectrum can be recorded. Prepare solutions of this concentration in hexane, ether, chloroform, or any solvent which has no absorption in the analyzed range. Determine the ratios of intensities for the bands of the keto- and enol forms and make up a series of solvents in the order of increasing content of the enol form.

(7) Evaluate the effect of the structural factors. Prepare 3-5% solutions of acetyl acetone and malonic ester in carbon tetrachloride and determine the ratio of intensities of the bands of the keto- and enol forms. Explain the differences between the spectra of these compounds.

Exercise 8. Hydrogen Bond

For the purposes of IR spectroscopic analysis of hydrogen bonds the convenient solvents are carbon sulphide and

carbon tetrachloride. To record spectra in a wide range of concentrations, cells of various thickness should be used (for instance, the cells with thickness from 2.5 to 0.05 mm are needed for the concentration range from 0.02 to 1.0 *M*).

Materials: *p*-chlorophenol, *p*-cresol, *p*-oxyanisole, *o*-nitrophenol, benzyl alcohol, carbon tetrachloride, dioxane, acetonitrile, pyridine and benzene.

Operational procedure:

(1) To study the effect of concentration, the IR spectra are recorded in the 4000-2500 cm^{-1} range for the carbon tetrachloride solutions of benzyl alcohol with the following concentrations: 0.5, 0.25, 0.10, 0.05, 0.025 and 0.01 *M*. The sample cell should be 1 to 2 mm thick and the reference cell should contain pure carbon tetrachloride. Explain the changes in the spectrum of benzyl alcohol in terms of formation of the intermolecular hydrogen bond. Identify the absorption bands ν_{OH} for the free OH groups and the OH groups involved in hydrogen bonding. For the latter band plot the intensity of ν_{OH} as a function of concentration.

Repeat the procedure with acetic acid instead of benzyl alcohol. Explain the recorded spectrum in terms of formation of the intermolecular hydrogen bond.

(2) For analysis of the temperature effect use a thermostatted cell with a constant thickness of 0.1-0.5 mm. Fill the cell with 0.5 *M* solution of benzyl alcohol in carbon tetrachloride. Record the spectrum in the 2500-4000 cm^{-1} range at 10° intervals from room temperature up to 65° C. Temperature should be raised slowly to prevent damaging of the cell windows, and at each temperature the cell should be kept for 10 min to reach equilibrium state. Explain the changes in the spectrum. Plot the intensities of the ν_{OH} bands as functions of temperature.

(3) For analysis of the effect of solvent record the IR spectra of the 0.01 *M* solutions of benzyl alcohol in the 2500-4000 cm^{-1} range using 1-2 mm cell and the following

solvents: carbon tetrachloride, benzene, acetonitrile, dioxane, pyridine.

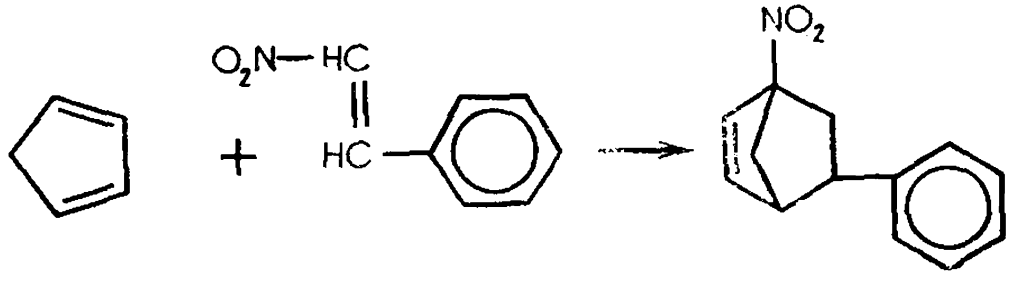
Record the spectrum of a liquid film of pure benzyl alcohol. For each solvent calculate the shift $\Delta\nu$ of the peak of the OH absorption band with respect to the peak of this band for the carbon tetrachloride solution. The shift $\Delta\nu$ can be regarded as an empirical parameter describing the capacity of the solvent for hydrogen bonding.

(4) To the effect of substituents prepare 0.125 *M* carbon tetrachloride solutions of the substituted phenols and record their IR spectra in the 2500-4000 cm^{-1} range.

Identify the absorption bands associated with the free OH groups and the OH groups involved in hydrogen bonding and calculate the relative areas of these bands (with a planimeter or by weighing). Arrange phenols in a series in the order of increasing hydrogen bond strength.

Exercise 9. Measurement of the Reaction Rate

The IR spectroscopy can be used for studies of the reaction kinetics if the starting compound and the reaction product have characteristic spectral absorption lines which can be distinguished in the spectrum. We shall study the diene synthesis reaction between cyclopentadiene and nitrostyrene. The reaction proceeds for 15-25 hours at 60-80° C without a solvent and with a sufficient cyclopentadiene excess (1 : 100):



The reaction conditions suggest that the reaction is of the pseudofirst order. The equation for the first-order reaction

can be written as follows:

$$K = \frac{2.3}{\tau} \log \frac{c_0}{c} \qquad (1)$$

Here K is the reaction rate constant, τ is the time of the reaction and c_0 and c are the concentrations of the starting compound at the beginning of the reaction and at the moment τ.

Beer's law yields

$$\frac{c_0}{c} = \frac{D_0}{D} \qquad (2)$$

where D_0 and D are the optical densities of the solution of the starting compound at the beginning of the reaction and at the moment τ.

Combining eqs. (1) and (2) we obtain

$$K = \frac{2.3}{\tau} \log \frac{D_0}{D}$$

Hence, the reaction rate constant can be calculated from the variation of the optical density of the reactant.

Operational procedure:

(1) Record the spectra of the starting compounds in chloroform and the spectrum of nitrostyrene in cyclopentadiene with reference to cyclopentadiene.

(2) Compare the spectra of nitrostyrene in various solvents; prepare several solutions of nitrostyrene in cyclopentadiene (0.06-0.02 *M*), record their spectra and compare them with the spectrum shown in Fig. 49.

(3) Plot the optical density D as a function of concentration c. A convenient analytical band is the antisymmetric stretching band of the nitro group which is the most distinct and strong one in the spectrum. For analysis of the reaction kinetics dissolve a weighed portion of nitrostyrene in cyclopentadiene (1 : 100, total volume 25 cm^3), record its spectrum with reference to cyclopentadiene and put the mixture into a thermostat at 60-70° C. At the beginning

take small (but sufficient for spectrum recording) samples of the mixture every two or three hours, and later reduce the interval of sampling to 1 hour*. Before recording the spectrum the sample should be kept at room temperature for 10-15 min. The changes in the spectra reflect the reaction process. For instance, the intensity of the absorption band ν_{as} of the conjugated nitro group at about 1530 cm^{-1} decreases and there appears the band ν_{as} of the unconjugated nitro group (of the reaction product) at a higher frequency (about 1565 cm^{-1}) whose intensity increases with time.

The optical density can be calculated from the decrease of the reactant content in the reaction mixture (the band ν_{as} for the conjugated nitro group) and from the increase in the content of the reaction product (the band ν_{as} for the unconjugated nitro group).

Several experiments should be made to measure τ, $T\%$, D and K.

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* It is not necessary to carry out the reaction to the end as 6 to 10 measurements are sufficient to calculate the reaction constant.

Chapter 3

Raman Spectroscopy

Similar to the IR spectroscopy, the Raman spectroscopy is used to determine the frequencies of molecular vibrations. These two spectroscopic techniques complement each other in analysis of the structures of organic compounds. When the light from a monochromatic source (laser, mercury lamp) is scattered by molecules the spectrum of the scattered light contains, apart from the frequency ν_0 of the incident light (the Rayleigh scattering), the Raman frequencies $\nu_0 - \nu_{vibr}$ and $\nu_0 + \nu_{vibr}$, the so-called satellites. The satellites with the frequency $\nu_0 - \nu_{vibr}$ are referred to as the Stokes lines (ν_s) and the satellites with the frequency $\nu_0 + + \nu_{vibr}$ are referred to as the anti-Stokes lines (ν_a). What is the origin of these lines? The diagram in Fig. 55 shows the relative arrangement of the initial (E_k) and final (E_n) energy levels for the Stokes (1), Rayleigh (2) and anti-Stokes (3) scattering.

There are three possible mechanisms of molecular light scattering.

(1) A molecule in the ground vibrational state with $v = 0$ is excited by an energy quantum $h\nu_0$ and returns to the state with $v = 0$ so that the scattered light has the same frequency as the incident light (Fig. 55, *2*).

(2) The excited molecule returns to a higher vibrational state so that the frequency of the scattered light is lower than that of the incident light (Fig. 55, *1*).

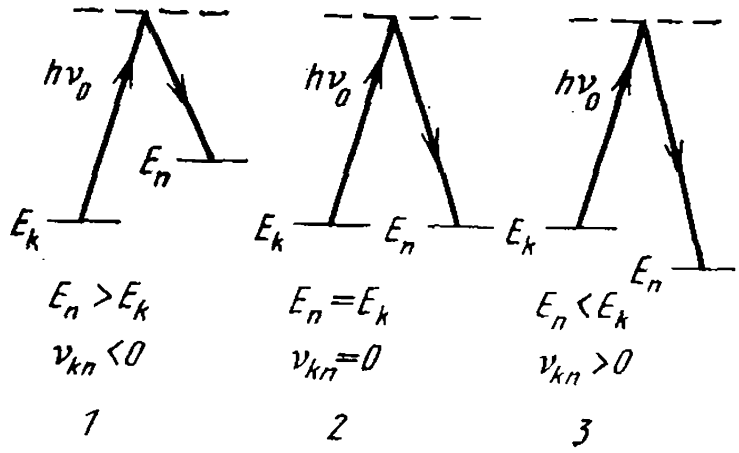


Fig. 55.
The relative positions of the initial (E_k) and final (E_n) energy levels for the Stokes (1), Rayleigh (2), and anti-Stokes (3) scattering.

(3) The initial vibrational state is an excited one and the final state is the ground state (Fig. 55, *3*). Then the frequency of the scattered light is higher than that of the incident light.

The properties of the electromagnetic radiation scattered by a material are determined by the polarizability α of the molecules. The polarizability describes the capacity of the electric charges to be displaced by external electric fields. If the electromagnetic wave induces in molecule the dipole moment p we can write

$$p = \alpha \cdot \varepsilon = \alpha \cdot \varepsilon_0 \cos 2\pi\nu_0 t \qquad (1)$$

where α is the electronic polarizability of the molecule, ε_0 is the wave amplitude and ν_0 is the wave frequency.

If the polarizability depends on the distance between the nuclei $\alpha = \alpha(q)$, the induced dipole moment will be given by the following formula which includes, apart from the Rayleigh term $c_0 \cos 2\pi\nu_0 t$, the Stokes and anti-Stokes terms:

$$p(q) = c_0 \cos 2\pi\nu_0 t + c_1 \left(\frac{d\alpha}{dq}\right)_{q=q_0} \cos 2\pi (\nu_0 + \nu_{\text{vibr}}) t + \\ + c_2 \left(\frac{d\alpha}{dq}\right)_{q=q_0} \cos 2\pi (\nu_0 - \nu_{\text{vibr}}) t \qquad (2)$$

Thus, the Raman scattering studies can yield the frequencies of molecular vibrations which are found as the difference between the frequencies of incident and scattered light. In contrast to the IR absorption spectra in which the band intensity is proportional to the squared derivative of the dipole moment with respect to the distance between the atoms, the intensity of the Raman lines I_R is proportional to the squared derivative of the molecular polarizability with respect to the distance between the nuclei:

$$I_R \sim \left(\frac{d\alpha}{dq}\right)^2_{q=q_0}$$

It can be seen that a molecule has a Raman spectrum only if its interaction with the incident light results in variation of its polarizability. For instance, diatomic homonuclear molecules which have no IR spectra (H_2, N_2, O_2) are Raman active since for them $d\alpha/dq \neq 0$. The

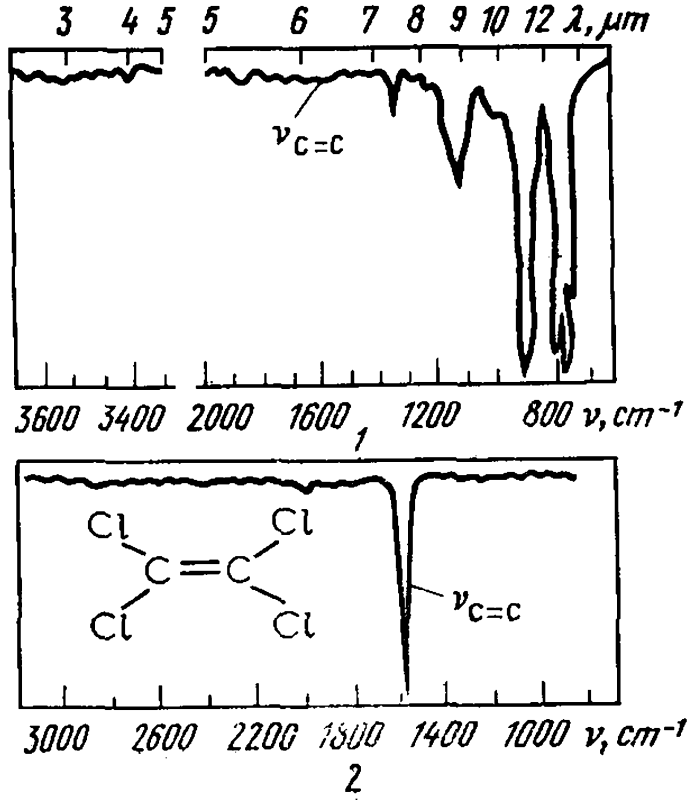


Fig. 56.
IR spectrum (1) and Raman spectrum (2) of tetrachloroethylene.

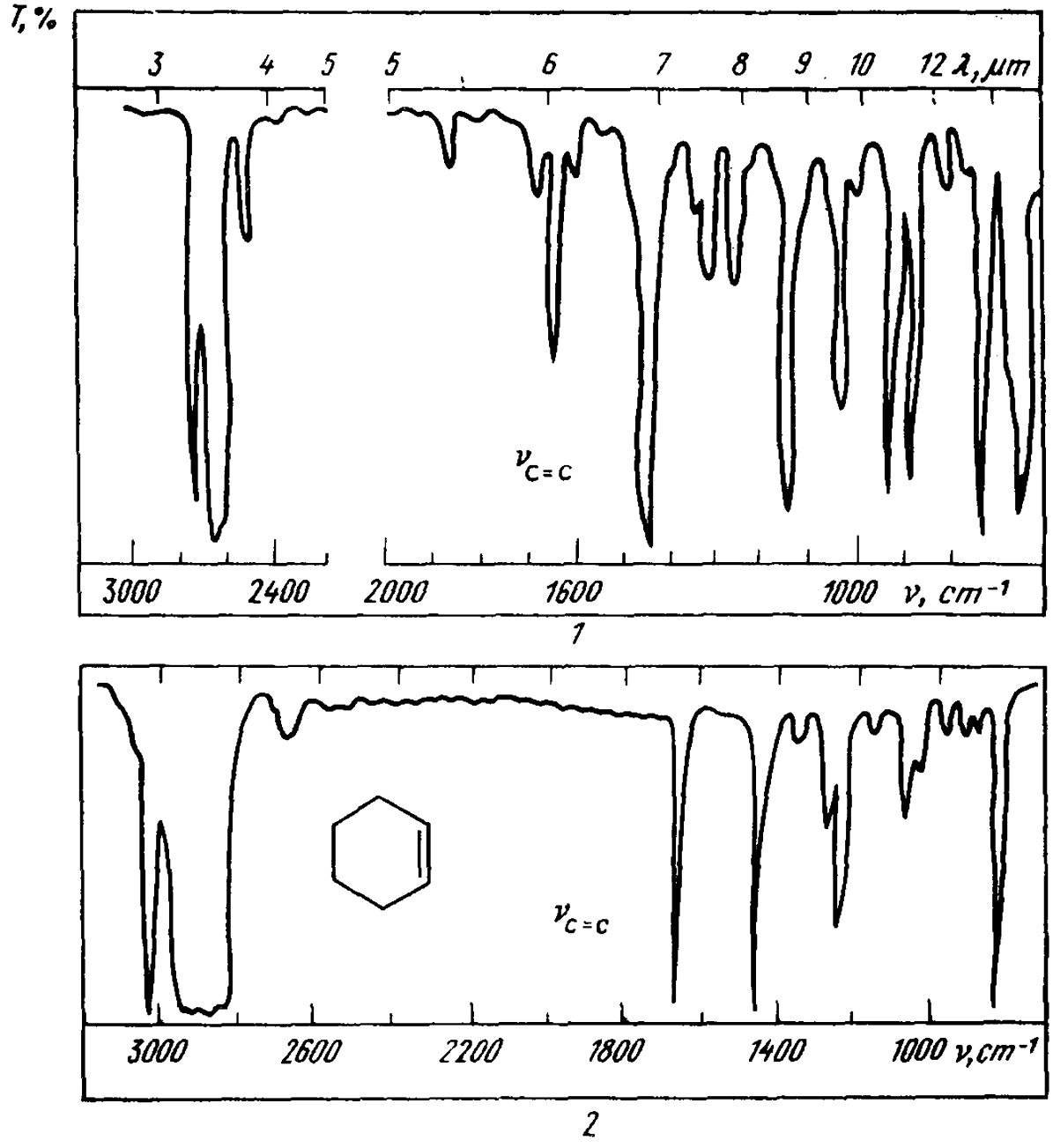


Fig. 57.
IR spectrum (1) and Raman spectrum (2) of cyclohexene.

IR and Raman spectra are different because the derivatives of the polarizability and of the dipole moment vary differently. Apart from the frequency and intensity, an important characteristic of the Raman spectra is the depolarization ratios of Raman lines.

The depolarization ratios ρ of Raman lines vary in the range $0 \leqslant \rho \leqslant 1$. The depolarization ratio is signifi-

cantly affected by many factors, such as the divergence of the incident light, the polarization effect of the optical elements of the spectrometer, etc. The depolarization ratio reflects the character of the electron density distribution and the conjugation effect in the organic molecules. A comparison of the IR and Raman spectra yields information on the symmetry of molecules. For instance, in ethylene the stretching vibrations of the double bond are symmetric so that the IR spectrum evidences no absorption; at the same time this vibration is distinctly reflected in the Raman spectrum; hence, the molecular structure is symmetric. These effects are illustrated by Figs. 56 and 57 presenting the IR and Raman spectra of tetrachloroethylene and cyclohexene. The Raman spectrum has a strong line associated with the stretching vibration of the double bond in tetrachloroethylene ($\nu_{C=C} = 1570\ cm^{-1}$) which is not reflected in the IR spectrum. The vibration of the less symmetric double bond in cyclohexene ($\nu_{C=C} = 1658\ cm^{-1}$) produces a weak band in the IR spectrum and a somewhat stronger band in the Raman spectrum. The Raman and IR frequencies for the same vibration (for instance, $\nu_{C=C}$ and ν_{NO_2}) are not necessarily identical owing to the specific features of the techniques. It should be noted that almost all frequencies of molecular vibrations can be found by analyzing the IR and Raman spectra. The Raman spectroscopic equipment operates in the visible spectral region which is an advantage compared to the IR spectroscopy where the IR-transparent materials should be used.

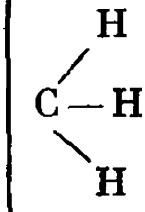
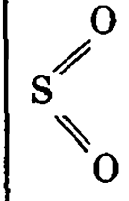
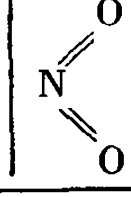
APPLICATIONS OF RAMAN SPECTROSCOPY TO CHEMISTRY

The Raman spectroscopy has wide-ranging potentialities. This technique is used, for instance, for analyzing the interatomic interactions, conformations, tautomerism, association, ionization, molecular symmetry, etc.

Identification of Compounds

Identification of organic compounds is carried out by making use of the characteristic frequencies and intensities of the vibrations of certain atom groups. For instance, the frequencies of vibration of the carbonyl, hydroxyl and nitrile groups are not much affected by the structure of the remaining part of the molecule (Table 17). These vibration frequen-

TABLE 17

Group X	Bonds	Alk—X		Ph—X		I (Ph—X)
		ν (cm^{-1})	I	ν (cm^{-1})	I	I (Alk—X)
—CH_3		2900	40	2900	50	1.25
—SOR	C—C	1000	—	—	—	—
	S=O	1048	48	—	—	—
—SO_2R		1135	100	1160	80	0.8
—COO	C=O	1745	14	1725	100	7.1
—CO	C=O	1719	14	1690	160	11.4
—COCl	C=O	1803	12	1770	170	14.1
—COBr	C=O	1812	14	1780	200	14.3
—COH	C=O	1729	13	1704	230	17.7
—Ph	C=C	1505	26	1600	700	27
—$CH=CH_2$	C=C	1642	30	1631	340	11.3
—$C\equiv CH$	C≡C	2118	75	2110	400	5.3
—CN	C≡N	2254	32	2231	330	10.3
NO_2		1380	35	1348	700	20

cies can, typically, be affected by such factors as the rigidity of chemical bonds, the conjugation effects, and other interactions.

Evaluation of the Degree of Conjugation. The data of Table 17 show that the intensities of the Raman lines for substituents in aromatic compounds are considerably higher than the intensities of the lines for the same groups in alkylated compounds. The intensity of the Raman lines is a reliable indicator of the degree of conjugation. The data given in Table 18 clearly demonstrate the effect of substituents on the intensities of lines for conjugated systems.

TABLE 18

THE EFFECT OF SUBSTITUENTS ON INTENSITIES OF THE RAMAN LINES IN COMPOUNDS PhX

X	I_{1600}	X	I_{1600}
H	35	CHO	200
OH	38	C=C	250
CCl_3	80	Ph	370
CN	150	C=C—C=C	1100
NR_2	170	C=C—CHO	1800
NO_2	200	C=C—NO_2	3200

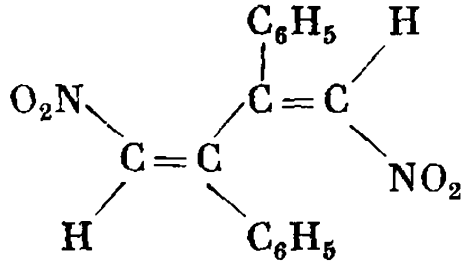
Table 18 gives the intensity coefficients for the characteristic line of the benzene ring in the 1570-1610 cm^{-1} range. A high line intensity with the resonance excitation is found for the ethers of the polyene acids, for instance, H_5C_2OOC—$—(CH=CH)_n—COOC_2H_5$ (in acetone). Lengthening of the polyene chain has little effect on the frequency $\nu_{C=O}$ but produces a rapid rise in the intensities $I_{C=C}$ and $I_{C=O}$ (see Table 19).

TABLE 19

n	$\nu_{C=C}$ (cm^{-1})	$I_{C=C}$	$\nu_{C=O}$ (cm^{-1})	$I_{C=O}$
0	—	—	1760	40
1	1664	300	1733	350
2	1643	5 000	1726	800
3	1620	30 000	1721	1800
4	1597	150 000	1717	6000
5	1572	$1.2 \cdot 10^6$	—	—

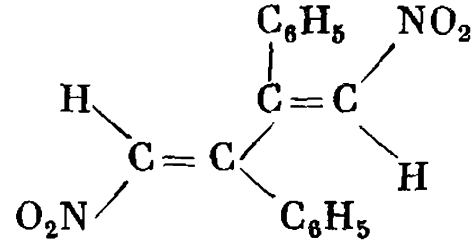
Molecular Conformations. The *cis-cis*-isomer (1) and the *trans-trans*-isomer (2) of 1,4-dinitro-2,3-diphenylbutadiene have different Raman spectra:

1.



$\nu_{as} = 1600$ (0.6)

2.



$\nu_{as} = 1585$ (2.6)

$\nu = 1615$ (0.9)

$\nu_s^{NO_2} = 1345$ (3.4)

The lines associated with the stretching vibrations of the double bonds and nitro group in the spectrum of the *cis-cis*-isomer have much lower intensities than those in the spectrum of the *trans-trans*-isomer. Therefore, the spectrum of the compound (1) contains no line associated with vibration of the nitro group. The spectrum of the compound (2) (with less spatial hindrance) contains high-intensity bands of the benzene ring (ν_{as}), the double bond, and the nitro group.

It should be noted that for the purposes of structural analysis a useful practice is to combine Raman spectroscopy with other spectroscopic techniques.

Chapter 4

Nuclear Magnetic Resonance Spectroscopy

The spectroscopic techniques discussed above are applied in the optical spectral regions. However, under certain conditions the radiofrequency range can also yield information on the fine features of the structure of organic and biological compounds. There are two main radiospectroscopic techniques—electron paramagnetic resonance (EPR) and nuclear magnetic resonance (NMR); the latter technique is widely used for structural analysis.

FUNDAMENTALS OF THE NMR TECHNIQUE

The atoms are known to be comprised of nuclei and electrons. The nuclei have positive charges which are multiples of the charge of the hydrogen nucleus (the proton). The nuclei of many isotopes have also the angular momentum known as the spin and characterized by the spin quantum number I $\left(I = 0, \frac{1}{2}, 1, 1\frac{1}{2}, 2, \ldots\right)$. Rotation of the charged nucleus is equivalent to a circular electric current and gives rise to the magnetic field directed along the rotation axis. Thus, the nucleus can be regarded as a micromagnet with the magnetic moment μ.

The magnetic moment of the nucleus is related to the spin by the following equation:

$$\mu = \gamma \cdot p = \gamma \left(\frac{h}{2\pi} I\right) \qquad (1)$$

where μ is the magnetic moment of the nucleus, p is the spin of the nucleus, γ is a constant describing the type of the nucleus (the gyromagnetic ratio) and h is Planck's constant.

The nuclei with even numbers of protons do not possess spins ($I = 0$) and their magnetic moment is zero. Therefore atoms with even mass and atomic numbers, such as ^{12}C, ^{16}O and ^{32}S have no magnetic properties and do not produce NMR signals. Other nuclei have nonzero spins ($I \neq 0$).

The nuclear magnetic moment is quantized, that is, its projection on an external uniform magnetic field H_0 can have any of $2I + 1$ discrete values determined by the magnetic quantum number m_I ($m_I = I, I - 1, \ldots, 0, \ldots \ldots, -I + 1, -I$). Each value of m_I corresponds to a certain energy level; the distance between the levels is constant and equal to $\mu H_0/I$. The nuclei which are most common in organic chemistry (^1H, ^{13}C, ^{15}N, ^{19}F, ^{31}P) have the spin $I = \frac{1}{2}$. In the external magnetic field such nuclei can be in two energy states—with the magnetic moment parallel $\left(m = \frac{1}{2}\right)$ or antiparallel $\left(m = -\frac{1}{2}\right)$ to the external magnetic field (Fig. 58). The distance between these levels is determined by the nuclear magnetic moment and the external field:

$$\Delta E = 2\mu H_0 = \gamma \frac{h}{2\pi} H_0 \qquad (2)$$

Since reorientation of spin is equivalent to transition from one energy level to another the process results in absorption or liberation of energy in the form of the electromagnetic radiation quantum $h\nu$:

$$\Delta E = h\nu = \gamma \cdot \frac{h}{2\pi} H_0 \qquad (3)$$

Hence we find the frequency

$$\nu = \frac{\gamma}{2\pi} H_0 \qquad (4)$$

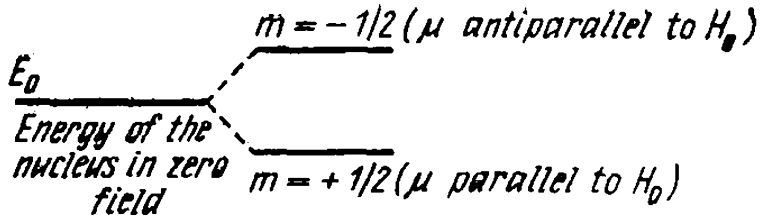


Fig. 58.

Splitting of the energy levels of the nuclei with spin $I = \frac{1}{2}$ in the magnetic field.

These transitions make possible the nuclear magnetic resonance which is observed when the nucleus is in the variable magnetic field H with the frequency satisfying the resonance condition (4). If there is no external magnetic field the energy levels of the nucleus coincide (the doubly degenerate state). At the normal temperature the population of the ground level with $m = +\frac{1}{2}$ is somewhat higher than that of the level with $m = -\frac{1}{2}$ but the difference is very small. This is due to the fact that the thermal motion energy kT is much higher than the difference of the energy levels given by eq. (3). The difference between the level populations is not more than about 10^{-5} of the total number of magnetic nuclei. Absorption of the radiofrequency energy results in equalization of the populations of both levels. The system of magnetic nuclei should then return to the equilibrium state because otherwise the level populations will be equal and the radiofrequency radiation will not be absorbed (the saturation effect). The spontaneous transition to the equilibrium state by radiation of the absorbed energy is not sufficient for eliminating saturation since it is a long-time process. The nuclei return to the equilibrium state via two main mechanisms—the spin-spin and spin-lattice relaxation. The time T_2 of the spin-spin relaxation is determined by the rate of relaxation to the equilibrium

state owing to the interaction in the spin system while the spin-lattice relaxation time T_1 is determined by the rate of relaxation to the thermal equilibrium between the system of nuclear spins and other degrees of freedom (related to the lattice) of the sample. In liquids T_1 and T_2 are approximately 1 s, which corresponds to the resonance line width $\Delta\nu$ of about 1 Hz ($\Delta\nu \sim 1/T_1$). If the sample contains paramagnetic molecules or atoms the time T_1 decreases (the spectral line widens) to such an extent that the line frequently becomes undistinguishable. The same factor determines the widening of the lines of the protons in nuclei possessing a quadrupole moment (for instance, ^{14}N).

The fundamental NMR parameters are the chemical shift (δ, τ) and the spin-spin coupling constant (J).

CHEMICAL SHIFT

When an external constant magnetic field is applied to an atom its electrons interact with the external field H_0 inducing the magnetic field $H = -\sigma H_0$ of the opposite sense.

The dimensionless constant σ known as the shielding constant is independent of H_0 but depends on the chemical (electronic) environment. Owing to shielding the nucleus is affected by the effective field

$$H_{\text{eff}} = H_0 - \sigma H_0 = H_0 (1 - \sigma) \qquad (5)$$

The shielding of nuclei results in a decreased distance between the energy levels so that for the same frequency of the applied field the resonance for the shielded nuclei is observed at a higher field than for the unshielded nuclei.

A given sample always contains several groups of nuclei of the same isotope (for instance, protons) which are present in molecules of one or several compounds and have different shielding constants. Such groups of nuclei produce

separate signals in the NMR spectrum. The shift of the NMR signal produced by the difference in the shielding constants due to chemical environment is referred to as the chemical shift. The chemical shift is measured typically in frequency units (Hz) but then it depends on the applied field. Therefore, in NMR spectroscopy the chemical shifts are given with respect to a reference compound as parts per million (ppm) of the applied field or frequency:

$$\delta = \frac{H_s - H_{ref}}{H_0} \cdot 10^6 \qquad (6)$$

$$\delta = \frac{\nu_s - \nu_{ref}}{\nu_0} \cdot 10^6 \qquad (7)$$

where H_s and ν_s are the resonance field and frequency for the sample, H_{ref} and ν_{ref} are the resonance field and frequency for the reference, and H_0 and ν_0 are the applied field and its frequency.

For protons of most compounds the chemical shifts vary from 0 to 10 ppm (Fig. 59). The compounds used as references contain one proton or a group of equivalent protons (chloroform, cyclohexane, benzene, dioxane, water). The reference compound is either mixed with the sample solutions (the internal standard) or is put into a separate sealed tube (the external standard). In the latter case a correction should be made taking into account the difference between

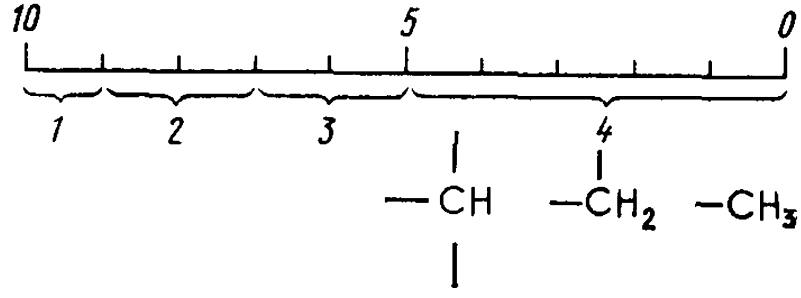


Fig. 59.
Proton chemical shifts: *1*—aldehydes, *2*—aromatic compounds, *3*—olefins, *4*—aliphatic compounds.

the bulk diamagnetic susceptibilities of the sample and the standard.

Currently, the internationally accepted reference compound is tetramethylsilane (TMS) which has been chosen as such for the following reasons: firstly, it has a single narrow signal at a field higher than is the case for most organic compounds and, secondly, it has a low reactivity and solvents exert weak effect on the position of its signal. The chemical shift for the TMS proton is taken to be zero. In the τ scale of chemical shifts TMS is given the chemical shift of 10. The chemical shift can easily be converted from one scale to another:

$$\tau = 10 - \delta \qquad (8)$$

In molecules the shielding of nuclei is affected by the local diamagnetic and paramagnetic fields due to motion of the electrons of the atom, by the diamagnetic and paramagnetic fields of the neighbouring atoms, and by the fields produced by the interatomic currents. The local field at the nucleus is always reduced by diamagnetic shielding due to the atom's own electrons. The degree of electron shielding depends on the electron density and frequently correlates with the electronegativity of the neighbouring atoms if other contributions to the shielding are small.

The signal of the protons of acetylene is shifted upfield by 2.96 ppm compared with that of ethylene ($\delta = 5.84$ ppm) owing to the shielding effect of the paramagnetic currents. In the molecules with rigid configurations the fields of electronic currents may give rise either to shielding or deshielding of the nuclei. Such effects depend on the orientation of the nuclear spin with respect to the induced fields and are known as the anisotropic effects. The anisotropic effects should be taken into account in analysis of the chemical shifts of protons located close to double or triple bonds.

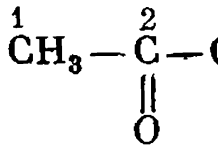
The aromatic molecules contain large closed overlapping π-electron systems in which an external field produces circular diamagnetic currents. These currents give rise to a magnetic field perpendicular to the plane of the aromatic ring which has an anomalously high shielding effect on any group of protons above or below the plane of the ring. For the aromatic protons this field has a deshielding effect increasing the external field. This effect accounts for the downfield shift of the signal of the benzene protons ($\delta = 7.27$ ppm) by 1.43 ppm compared with the signal of the protons of ethylene.

The electron density in a molecule can be estimated from the chemical shift value for the protons. It should be noted that the standard values of the proton chemical shifts for the functional groups are only tentative ones. For some classes of organic compounds (acyclic alkanes and alkenes) the calculations making use of the additive scheme can yield more accurate values of the chemical shifts for protons of various groups and which are closer to the experimental results.

CALCULATIONS OF CHEMICAL SHIFTS OF PROTONS MAKING USE OF THE ADDITIVE SCHEME

In the additive scheme the chemical shifts of protons linked to carbon atoms are calculated by adding empirical constants for given substituents to the basic value T_0 used as a reference. The basic element is taken to be a hypothetical methane ($T_0 = 0.824$ ppm). To make use of the additive scheme the atoms of the carbon skeleton of the molecule are enumerated starting from the atom whose chemical shift has to be determined. The constants for the substituents at the carbon skeleton are given in the Appendix (Table 2).

Let us calculate the proton chemical shift of the CH_3 group of acetone:



$\delta = T_0 + T_2 + T_{11}$ (see Table 2)

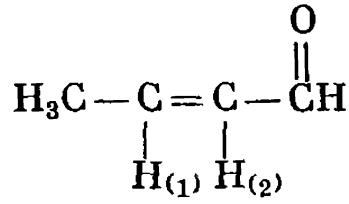
$$\delta = 0.824 + 0.296 + 0.986 = 2.106 \text{ ppm}$$

This value is in a good agreement with the experimental results.

The chemical shift of protons at the double bond can be calculated from the following formula:

$$\delta_H = (5.25 + Z_{hem} + Z_{cis} + Z_{trans}) \text{ (ppm)}$$

where 5.25 ppm is the basic chemical shift value and Z parameters are the increments for the substituents given in Appendix (Table 3). This formula yields the following value for the chemical shift of protons at the double bond of the aldehyde



$$\delta_{H_{(1)}} = 5.25 - 0.22 + 1.06 = 6.09 \text{ ppm}$$

$$\delta_{H_{(2)}} = 5.25 + 0.45 + 1.06 = 6.76 \text{ ppm}$$

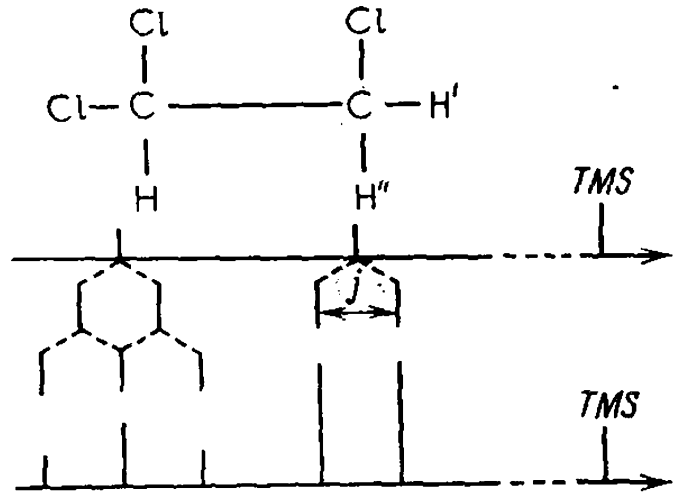
The NMR spectroscopic results for these protons are

$$\delta_{H_{(1)}} = 6.13 \text{ ppm} \quad \text{and} \quad \delta_{H_{(2)}} = 6.68 \text{ ppm}$$

SPIN-SPIN COUPLING

Apart from the chemical shift, the spin-spin coupling of the nuclei also yields valuable data on the structure of organic compounds. The spin-spin coupling is caused by magnetic interaction of the chemically nonequivalent

Fig. 60.
Splitting of signals in the NMR spectrum of 1,1,2-trichloroethane.



nuclei via the bonding electrons. The spin-spin coupling produces splitting of lines in the spectrum and its magnitude falls off rapidly with distance. Let us discuss this effect.

The spectrum in Fig. 60 has two signals splitting of which is due to the interaction between the protons located at neighbouring carbon atoms and having different chemical shifts. The proton H is located at the carbon atom bound to two electronegative chlorine atoms so that its signal should be in a lower field than the signals of the protons H′ and H″. Let us now take into account the contribution of the spin-spin interaction of the nuclei. The proton H with its own magnetic field produces an effect on the protons H′ and H″ via the bonding electrons (indirect interaction). Since the spin of the proton H has two permitted orientations in the external magnetic field it can produce two additional fields at the site of the proton H′ (H″) (producing a downfield and an upfield shift) so that one signal of the proton H′ (H″) is replaced by a doublet. The distance (in Hz) between the two lines of the doublet is a measure of the strength of interaction between the two nuclei and is called the spin-spin coupling constant J. The signal of H″ is also split into a doublet, both doublets (for H′ and H″) being identical.

The spins of the nuclei H′ and H″ can be independently parallel or antiparallel to the field and can also affect the

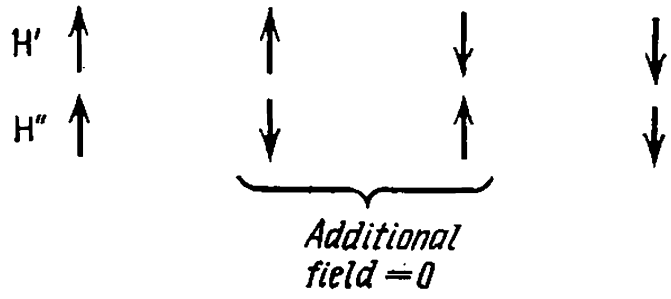


Fig. 61.
Alignment of spins of CH_2 protons.

proton H. If the spins of H′ and H″ are both parallel or antiparallel to the external field their fields are added and increase or decrease the external field; if the spins of H′ and H″ are antiparallel the sum of their fields is zero (Fig. 61).

All the possible spin orientations for the protons H′ and H″ have the same probabilities and thus the signal of the proton H is split into a triplet where the intensity of the central line (the additional field is zero) is twice that of the side lines.

The separations of the neighbouring lines in the doublet and the triplet are identical being equal to the spin-spin coupling constant J for the protons of the neighbouring groups. The integral intensities of the doublet and triplet are proportional to the number of protons producing these signals, that is, their ratio is 2 : 1. The number M of lines in the multiplet due to the spin-spin coupling is given by the following equation*:

$$M = 2NI + 1 \tag{9}$$

where I is the spin quantum number and N is the number of the neighbouring magnetically equivalent nuclei. If the interacting nuclei have $I = \frac{1}{2}$, eq. (9) is simplified:

$$M = N + 1 \tag{10}$$

* Eq. (9) is valid when the difference between the chemical shifts of the interacting nuclei is much larger than the coupling constant.

The chemical shifts of protons with the spin-spin splitting are found as the distance from the centre of the multiplet to the reference signal. The magnitude of the spin-spin coupling constant is independent of the external magnetic field H_0; it is determined by the nature of the interacting nuclei, the number and character of the bonds between them, and the geometry of the molecule.

It should be noted that determination of the number of protons making a contribution to a signal and application of the simple rule (eq. (10)) for calculation of the signal multiplicity are not difficult if the difference between the chemical shifts is larger (by a factor of 6 or more) than the spin-spin coupling constant.

APPLICATION OF NMR SPECTROSCOPY TO STRUCTURAL ANALYSIS

Though it is highly effective in structural studies of organic compounds, NMR spectroscopy cannot replace IR and UV spectroscopy and the data of these techniques complement each other. We shall discuss here some applications which illustrate the scope of NMR spectroscopy.

The spectrum of the proton magnetic resonance (a special case of NMR) is a number of peaks recorded on a spectrogram. Each peak or, sometimes, a number of peaks, represents the NMR signal of the nucleus (hydrogen atom) which is being studied.

The heights, widths and areas of the peaks, the magnetic fields at which they are found (the chemical shifts) and other parameters are determined by the magnetic and electric properties of the nuclei under study and by the properties of the atoms, groups of atoms and molecules surrounding these nuclei. Thus, the NMR spectra reflect the structure of materials.

The structural data are obtained from an NMR spectrum by interpreting it. The number of problems given below is too small to illustrate the full range of NMR applications but they make it possible to get acquainted with the types of information provided by the NMR spectra. It should be noted that the problems deal with spectra of relatively simple compounds. Interpretation of the spectrum of a complex compound is sometimes very difficult, particularly, if the spectrum is not fully resolved and the signals of various hydrogen atoms overlap (fully or partially). Under such circumstances a computer-calculated spectrum should be compared with the recorded spectrum. To simplify the recorded spectra, such techniques as the double nuclear resonance, isotope substitution and other methods are used. However, the problems given below illustrate the basic techniques used for interpretation of the NMR spectra in many practical applications.

The problems deal only with the NMR spectra of hydrogen atoms. The chemical shifts are given with respect to the signal of tetramethylsilane $(CH_3)_4Si$ which is upfield from the signals of most compounds.

Identification of Compounds. Let us analyze the spectrum of benzyl acetate $C_6H_5CH_2OC(=O)CH_3$ (Fig. 62). The spectrum has three distinct signals—$\delta_1 = 2.06$ ppm, $\delta_2 = 5.08$ ppm and $\delta_3 = 7.31$ ppm.

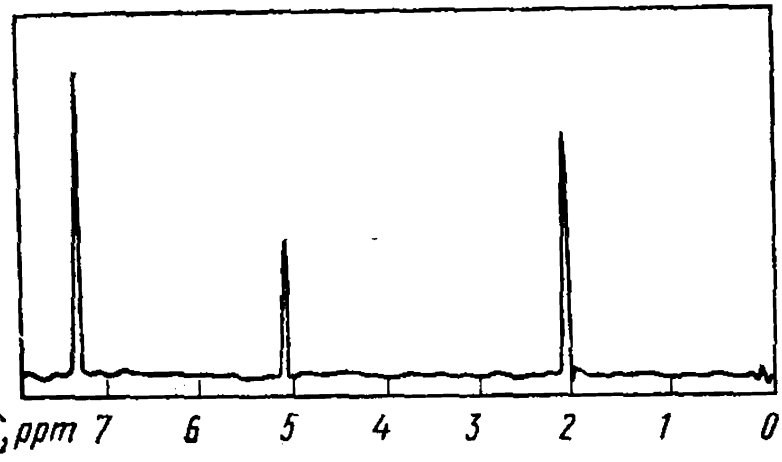
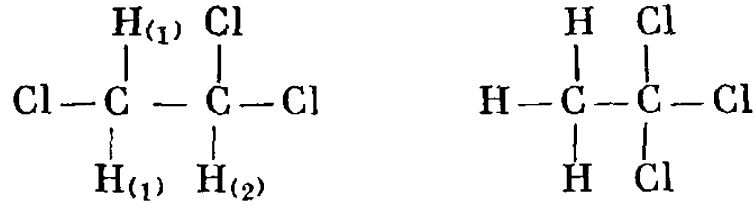


Fig. 62.

It should be noted that analysis of any NMR spectra must take into account the fact that the integral intensity of the signals (the area of the peaks) is proportional to the number of protons of the substituents. Therefore, the high-intensity signal with $\delta_3 = 7.31$ ppm should be assigned to the protons of the benzene ring. The signal with $\delta_2 = 5.08$ ppm which is shifted upfield from δ_3 and has the lowest intensity is assigned to the protons of the methylene group CH_2. A somewhat higher value of the chemical shift δ_2 compared with its typical value (see Fig. 59) is attributed to the electronic effect of the substituents (oxygen and benzene ring) which have a deshielding effect on the CH_2 group. The signal with $\delta_1 = 2.06$ ppm should be assigned to the protons of the methyl group; its value is close to the characteristic value.

Molecular Conformation. The structure of the compound $C_2H_3Cl_3$ can be determined from its NMR spectrum given in Fig. 63. This compound can have two structures

1. 2.



The structure (2) contains three magnetically equivalent protons which should produce a singlet in the NMR spectrum. The spectrum of the structure (1) should be much more complicated since this structure contains two equivalent protons $H_{(1)}$ and the proton $H_{(2)}$. Owing to the spin-spin coupling the proton $H_{(2)}$ under the effect of two equivalent protons $H_{(1)}$ should produce a triplet signal while the proton $H_{(1)}$ under the effect of the proton $H_{(2)}$ should produce a doublet signal. The chemical shift for the proton $H_{(2)}$ should be larger than that for the proton $H_{(1)}$ since at the respective carbon atom there are two electro-

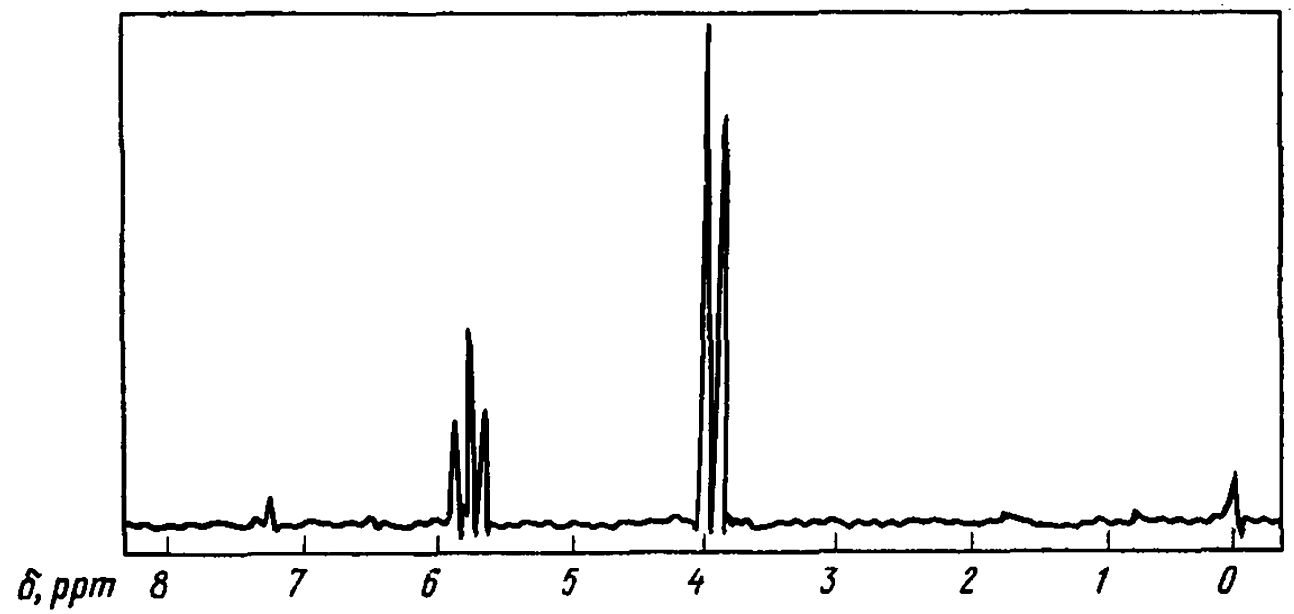


Fig. 63.

negative chlorine atoms. Thus, the above analysis of the spectrum indicates that the compound has the structure (1).

Let us now calculate the chemical shifts for the protons $H_{(1)}$ and $H_{(2)}$ of the structure (1) using the additive scheme and the Table 2 given in Appendix:

$$\delta_{H_{(1)}} = T_0 + T_1 + T_{17} + T_{18} + T_{18}$$

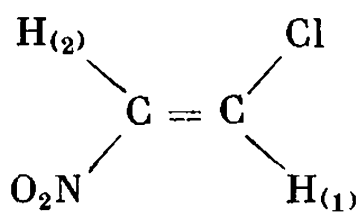
$$\delta_{H_{(2)}} = T_0 + T_1 + T_{18} + T_{17} + T_{17}$$

$$\delta_{H_{(1)}} = 0.824 + 0.363 + 2.175 + 0.303 + 0.303 = 3.97 \text{ ppm}$$

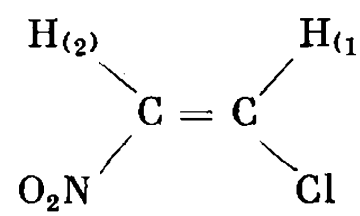
$$\delta_{H_{(2)}} = 0.824 + 0.363 + 0.303 + 2.175 + 2.175 = 5.84 \text{ ppm}$$

These values are in a fairly good agreement with the spectral data.

1-Nitro-2-chloroethene forms the following two isomers:



trans-isomer



cis-isomer

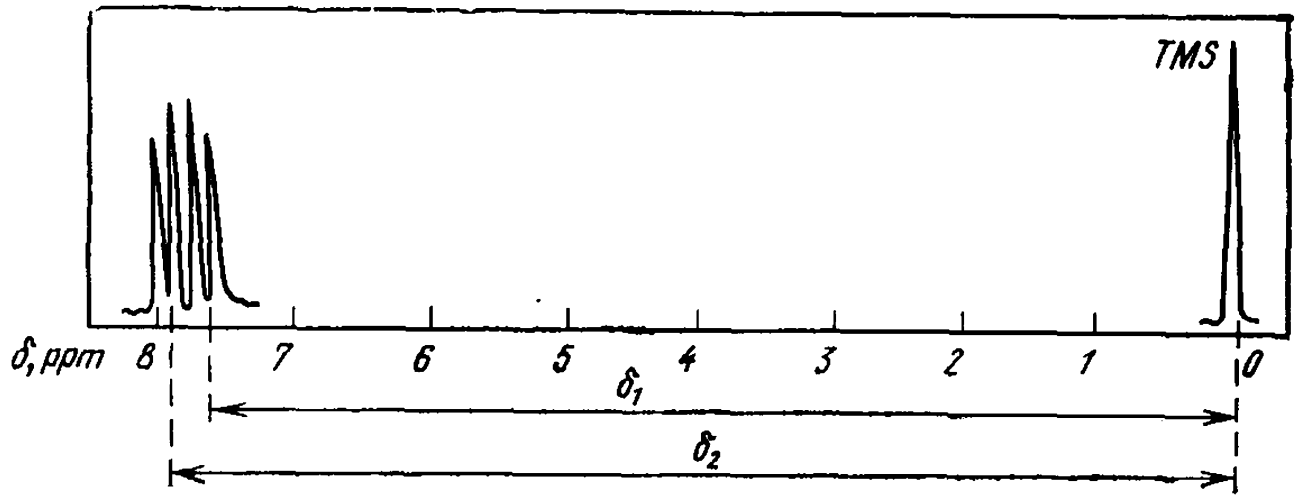


Fig. 64.

Owing to the spin-spin coupling with the proton $H_{(2)}$ the signal of the proton $H_{(1)}$ is a doublet. For the same reason the signal of the proton $H_{(2)}$ is also a doublet so that the NMR spectrum is a quartet (Fig. 64).

The chemical shift for each proton is found as the distance from the TMS signal to the centre of the doublet. For the *trans*-isomers the spin-spin coupling constant varies typically from 11 to 18 Hz and for the *cis*-isomers from 4 to 12 Hz. For both isomers the spin-spin coupling constants decrease if the substituents at the double bond are strong electron acceptors (NO_2, halogens, etc.). In our case $J = 11.7$ Hz, that is, the NMR spectrum is produced by the *trans*-isomer.

The NMR techniques are also used to study the hindered internal rotation of molecules, the keto-enol tautomerism and other tautomeric transformations, the proton exchange rates, the stereochemistry of organic compounds, etc. The temperature dependence of the NMR spectra is used to determine the energy barriers of rotation, the rate of transformation of the spatial conformers and so on. The temperature effect on the NMR spectra can be illustrated by the following examples. At 25° C the signals of the nonequivalent methyl groups of N,N-dimethylformamide are found at 2.95

and 2.80 ppm, and at 120° C they merge into one peak. At room temperature cyclohexane has one peak which is split into two with decreasing temperature.

PROBLEMS IN NMR SPECTROSCOPY

Problem 1. Fig. 65 presents the NMR spectrum of a mixture of the following compounds—tetramethylsilane, cyclohexane, benzene and chloroform—which are used as reference compounds. Identify the signals of each of the compounds and determine their content in the mixture.

Answer. Tetramethylsilane—$\delta = 0$; cyclohexane—$\delta = 1.43$ ppm; benzene—$\delta = 7.22$ ppm; chloroform—$\delta = 7.33$ ppm.

The peak area is proportional to the number of the hydrogen atoms. As the line widths are approximately the same, the peak areas are proportional to the peak heights. The ratio of intensities in the spectrum is 2 : 2 : 2 : 1. The ratio of hydrogen atoms for these compounds is 12 : 12 : 6 : 1. Hence the ratio of the components in the mixture is 1 : 1 : 2 : : 6.

Problem 2. A compound contains a methyl and a methylene group and is soluble in water, methyl alcohol, ethyl alcohol, carbon tetrachloride, chloroform, benzene and acetone. Which of the above solvents can be used for recording

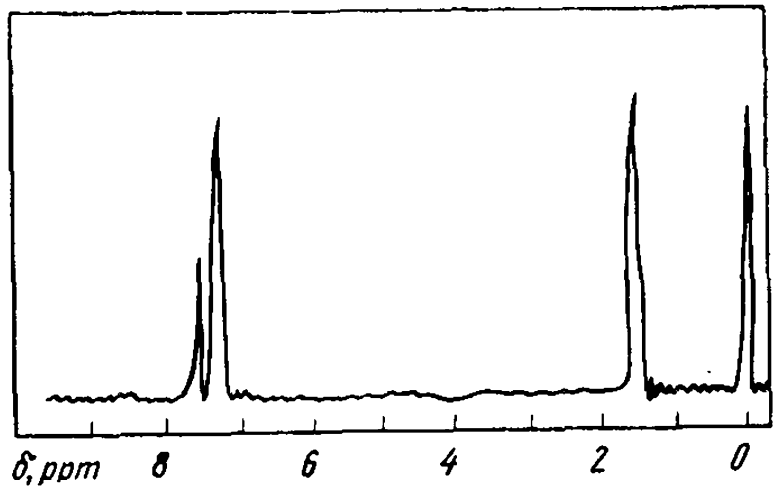


Fig. 65.

the NMR spectrum of the compound, and which cannot?

Answer. Carbon tetrachloride, chloroform and benzene can be used for recording the spectrum as the signals of their protons are far from the signals of the compound (and carbon tetrachloride contains no protons at all). The signals of the water protons are rather far from those of the groups CH_2 and CH_3 ($\delta_{H_2O} = 4.75$ ppm) but the signal of the water protons is very strong and can partially overlap with the signals of the compound under study. Methyl and ethyl alcohols and acetone are not suitable since they contain the same groups as the compound under study.

Problem. 3. At room temperature cyclohexane has one peak in the NMR spectrum. When the temperature decreases to —70° C the signal widens and at —100° C it splits into two distinct peaks. Explain this effect.

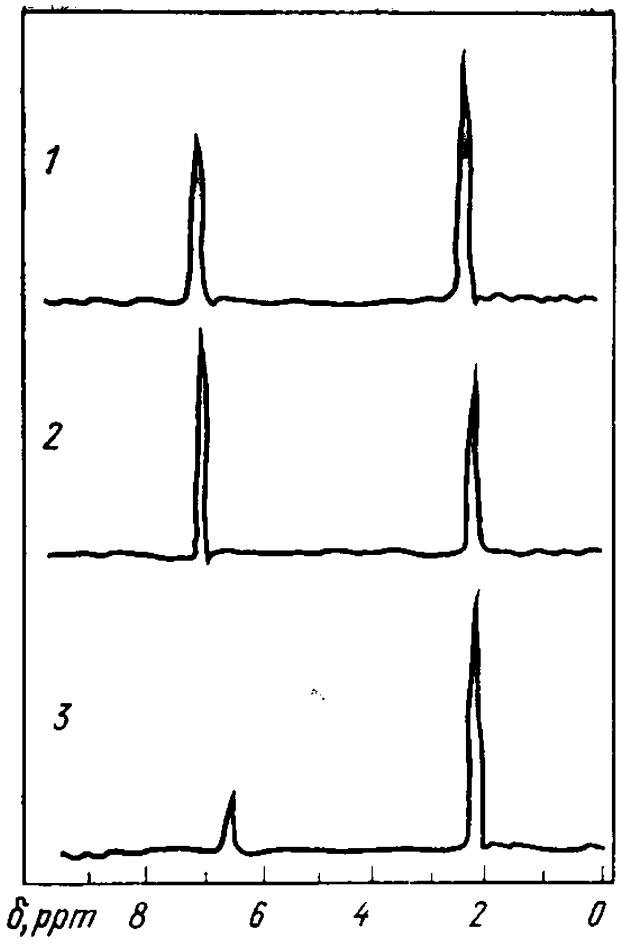
Answer. Cyclohexane has two conformations (chair and boat conformations) in which a distinction is made between two types of hydrogen atoms—the axial ones and the equatorial ones. At room temperature there occur very rapid transformations of one conformation into another, and the NMR spectrum recorded under these conditions is an averaged one since the equatorial protons of one conformation become the axial ones in the other conformation and *vice versa*. At low temperatures transformations of one conformation into another become slower and the separate signals of the equatorial and axial protons are observed.

Problem 4. The compounds $CHCl_2—CHCl_2$ ($\delta = 6$ ppm) and $CCl_3—CH_2Cl$ ($\delta = 3.9$ ppm) produce single NMR signals owing to the fact that their hydrogen atoms are chemically equivalent. Explain the difference between the chemical shifts for these compounds.

Answer. Halogens shift the proton signal downfield and the shift is the larger the larger the number of halogen atoms.

Problem 5. Toluene, *p*-xylene and mesitylene have two peaks each in their NMR spectra. Assign the spectra shown in Fig. 66 (*1*, *2* and *3*) to these compounds.

Fig. 66.



Answer. The signal with δ = 2 ppm is produced by the protons of the methyl group and the signal at about 7 ppm by the aromatic protons. As the lines have approximately the same widths, the ratios of the peak areas are 3 : 2, 3 : 5 and 3 : 1 in the first, second and third spectra, respectively. Hence, the spectra can be assigned as follows: *1*—*p*-xylene, *2*—*p*-toluene, *3*—mesitylene.

Problem 6. The NMR spectrum of the compound with the formula $C_2H_4Br_2$ contains a doublet with δ = 2.5 ppm and a quartet with δ = 5.8 ppm having the peak area ratio of 3 : 1. Determine the structure of the compound.

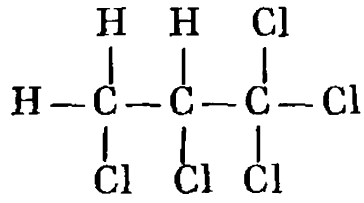
Answer. The only possible structure is that of 1,1-dibromoethane since, according to the multiplicity rule, the protons of the methyl group should give a doublet and the protons of the methine group should give a quartet with the peak area ratio of 3 : 1.

Problem 7. Identify the structures of the compounds $C_3H_3Cl_5$ (1) and $C_3H_5Cl_3$ (2) with the following NMR spectra:

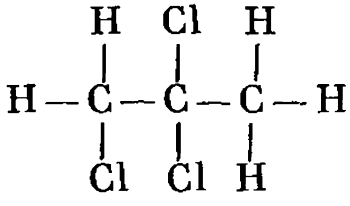
(1) Triplet ($\delta = 4.52$ ppm) and doublet ($\delta = 6.07$ ppm) with the peak area ratio of 1 : 2.

(2) Singlets ($\delta = 2.20$ ppm and $\delta = 4.02$ ppm) with the peak area ratio of 3 : 2.

Answer. The triplet with $\delta = 4.52$ ppm and the doublet with $\delta = 6.07$ ppm indicate that the methine group (1H) has a neighbour with two protons (2H). Hence the compound (1) has the following structure:



The singlets in the spectrum of the compound (2) indicate that two proton groups are separated by an aprotic group making spin-spin coupling impossible. Thus, the compound (2) has the following structure:



Problem 8. Fig. 67 gives two spectra for the compounds with the same empirical formula $C_8H_{10}O$. Determine the structures and explain the differences in the chemical shifts.

Answer.

1. $C_6H_5—CH_2—O—CH_3$ 2. $C_6H_5—O—CH_2—CH_3$

In the compound (1) the oxygen atom is linked to the groups CH_2 and CH_3 and therefore both peaks are shifted downfield (the chemical shifts are larger) and there is no spin-spin coupling between the protons of these groups. In the compound (2) the oxygen atom affects the group CH_2 (downfield shift of the peak) and the group C_6H_5.

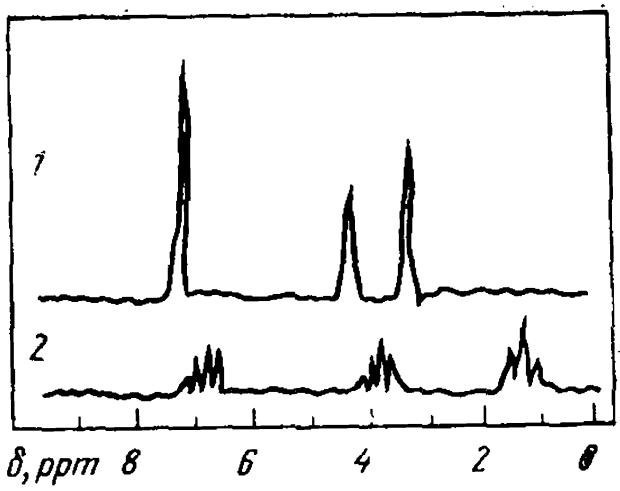


Fig. 67.

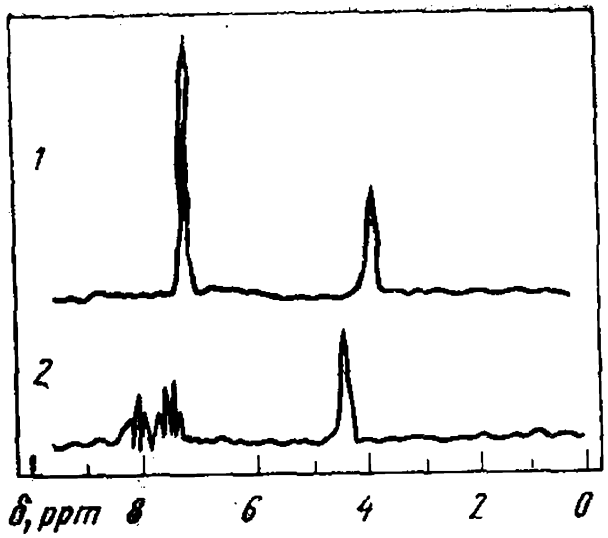


Fig. 68.

The aromatic protons become nonequivalent and the signal is split into a multiplet owing to their coupling.

Problem 9. Fig. 68 presents the NMR spectra of two compounds with the empirical formula C_8H_7OCl. Determine their structures.

Answer.

1. $C_6H_5—CH_2—COCl$ 2. $C_6H_5—CO—CH_2Cl$

The signals with the chemical shift of 7-8 ppm are typical of the aromatic ring. The multiplet indicates in the second case the presence of a substituent which does not affect the protons of the ring (singlet), and the singlet at 4 ppm shows that other protons are at one carbon atom.

Problem 10. Fig. 69 presents the NMR spectrum of the compound C_7H_8SH (δ = 7.2, 3.27, and 2.30 ppm). Determine the structure of the compound.

Answer. $CH_3C_6H_4SH$.

The signal with δ = 7.2 ppm is given by the protons of the benzene group, the singlet with δ = 2.30 ppm should be assigned to the methyl group (the CH_3 groups of toluene, xylenes and mesitylene have δ = 2.2-2.3 ppm), and the proton of the SH group gives a signal at δ = 3.27 ppm

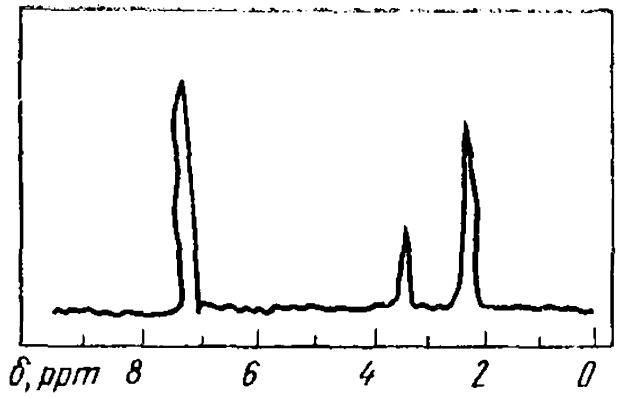


Fig. 69.

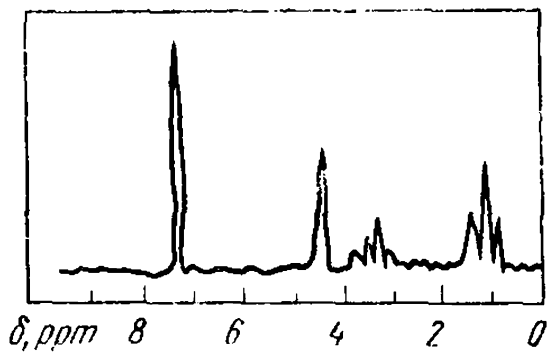


Fig. 70.

since the chemical shifts of the proton of the mercapto group in thiophenols are about 3.5 ppm.

Problem 11. Assign the NMR spectrum shown in Fig.70 to one of the following two structures:

1. $CH_3C_6H_4—OCH_2CH_3$ 2. $C_6H_5CH_2OCH_2CH_3$

Answer. The structure (1) is not suitable as the spectrum does not contain the signal of the protons of the methyl group at the aromatic ring (about 2 ppm). Moreover, the aromatic protons of the compound (1) are not equivalent and hence they should produce a multiplet at about 7 ppm. The compound has the structure (2).

Chapter 5

Dipole Moments

The dipole moment technique is used in modern chemistry mostly for determination of the type of a chemical bond (polar or covalent), molecular geometry (isomerism, valence angles, etc.), rotation of atomic groups, mutual effects of atoms and groups (mesomeric electron shift, ortho effect, etc.), properties of complexes and so on.

NATURE OF THE CONSTANT DIPOLE MOMENT

A dipole is a system of two opposite charges with equal magnitudes ($+e$ and $-e$) separated by a distance r, and its dipole moment is the product $\mu = er$. The dipole moment is a vector; in chemistry it is assigned the direction from the positive charge to the negative one. The dipole moments are measured in Debyes (1 Debye $= 3.33564 \cdot 10^{-30}$ c.m.).

The forces which maintain the electrical asymmetry of molecules and thus give rise to a constant dipole moment can be fully analyzed only in terms of quantum chemistry. In classical terms the dipole moments of diatomic molecules and of some chemical bonds of polyatomic molecules should be attributed to the differences in the electronegativities of the respective atoms. Owing to this difference the pair of bonding electrons is shifted towards the atom with a higher electronegativity and the centre of negative charges (electrons) is shifted with respect to the centre of positive

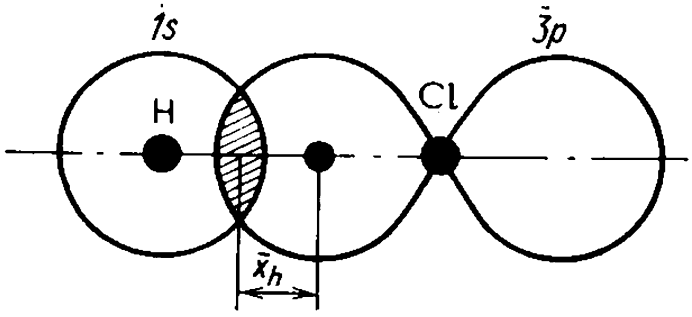


Fig. 71.
Origin of the homopolar dipole.

charges (nuclei). Such bonds are known as the polar bonds. In simple symmetric molecules containing two identical atoms (H_2, O_2, N_2, Cl_2 etc.) the centres of positive and negative charges coincide and the dipole moments are zero. If the atoms of a diatomic molecule have different electronegativities (HCl, HBr, etc.) the centres of the charges do not coincide; such polar molecules are electrically asymmetric and possess dipole moments. Complex polyatomic molecules which can have some polar bonds typically do not possess a dipole moment if they are centrally symmetric (CH_4, CCl_4, CO_2, SiF_6, C_6H_6, *p*-$C_6H_4Cl_2$, 1,3,5,-$C_6H_3(NO_2)_3$, etc.) and possess a dipole moment if they have no centre of symmetry (H_2O, NH_3, CH_3Cl, *o*-$C_6H_4Cl_2$, etc.).

However, the difference in the electronegativities of atoms is not the only factor giving rise to the dipole moment. A nonzero dipole moment can be due to different sizes of the atomic orbitals of the bond (homopolar dipole). Fig. 71 illustrates the origin of the homopolar dipole of the molecule HCl where bonding involves *1s* orbital of the hydrogen atom and $3p$ orbital of the chlorine atom. Since the orbitals have different shapes the centre of the negative charge is shifted towards the hydrogen atom by x_h (the positive charge centre is at the chlorine atom). The dipole moment of the homopolar dipole is $\mu_n = 2ex_h$ (the bond involves two electrons giving the factor 2 in the formula). The dipole moment increases with increasing difference between the sizes of the atoms in the molecule.

If bonding and nonbonding orbitals are hybridized as is the case for almost all real molecules the centres of the electronic densities of the hybrid orbitals do not coincide with the centres of the positive charge (that is, the nuclei). The resulting additional dipole moment known as the hybridization atomic dipole moment is, typically, rather large. For instance, the difference between the hybridization atomic dipole moments determines, to a considerable extent, the difference between the dipole moments of the C—H bonds in methane, ethylene and acetylene where the carbon atoms are in the hybridization states sp^3, sp^2 and sp, respectively.

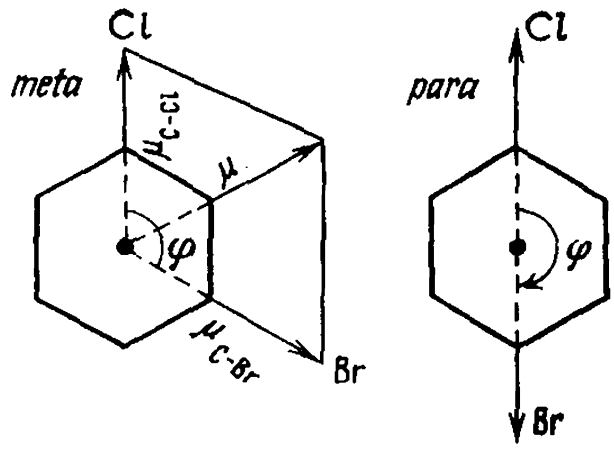
The atomic dipoles due to hybridization of the unshared electron pairs have especially large magnitudes. The dipole moment due to the asymmetry of nonbonding orbitals can be as large as 1.5-2*D* and in some cases (for instance, in acetone) it can have a considerable effect on the total dipole moment of the molecule.

DIPOLE MOMENTS OF BONDS AND GROUPS AND VECTOR ADDITION OF THEM IN POLYATOMIC MOLECULES

The dipole moments of polyatomic molecules depend on the nature of the atoms and bonds comprising the molecules and on their arrangement. In most applications of the dipole moments technique, calculations make use of the vector additive scheme which can be described as follows.

Each bond in a complex molecule can be ascribed its own dipole moment. The total dipole moment of the molecule is the sum of the dipole moments of the bonds. Since the dipole moments are vectors, the sum of the dipole moments of the bonds should be calculated according to the rule of vector addition. The dipole moments of molecules found as vector sums of the dipole moments of the bonds agree with the experimental results if the interactions between atoms and groups are not strong. Under such circumstances

Fig. 72.
Vector addition of the dipole moments for the *meta*- (1) and *para*-disubstituted (2) benzenes.



(1) (2)

the dipole moments of the bonds are additive and each bond can be ascribed a certain dipole moment which is approximately constant in various compounds.

Two vectors are added using the parallelogram of vectors (see Fig. 72). If two bonds with the dipole moments μ_1 and μ_2 are at an angle φ the total dipole moment is given by

$$\mu^2 = \mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cdot \cos\varphi \qquad (1)$$

For instance, two identical bonds with the opposite directions ($\varphi = 180°$) have $\mu = 0$.

For identical bonds ($\mu_1 = \mu_2$) eq. (1) yields

$$\mu^2 = 2\mu_1^2(1 + \cos\varphi) \qquad (2)$$

The dipole moments of most bonds reported in literature have been determined not by theoretical calculations (which are very difficult here) but by comparing the experimental data on the dipole moments of several compounds with the same bonds. Table 20 summarizes the dipole moments of various groups which will be used in further calculations.

Polyatomic substituents containing several polar bonds are typically assigned a common (total) dipole moment whose sense coincides with the direction of the bond C—X for the regular substituents (for instance, $-NO_2$, —CN,

TABLE 20

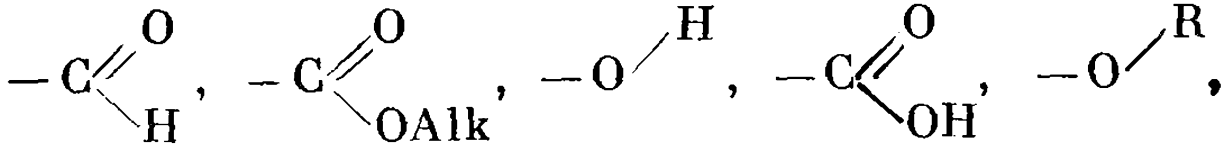
DIPOLE MOMENTS OF CHEMICAL GROUPS (in benzene, 25°C)*

Group X	μ_{CH_3-X} (D)	φ(deg.) **	$\mu_{C_6H_5-X}$ (D)	φ(deg.)
CH_3	0	0	0.37	0
CF_3	−2.32	0	−2.54	0
CCl_3	−1.57	0	−2.04	0
CN	−3.47	0	−4.05	0
CHO	−2.49	125	−2.96	146
$COCH_3$	−2.75	120	−2.96	132
COOH	−1.63	106	—	—
$COOCH_3$	—	—	−1.83	110
F	−1.79	0	−1.47	0
Cl	−1.87	0	−1.59	0
Br	−1.82	0	−1.57	0
I	−1.65	0	−1.40	0
OH	—	—	1.55	90
OCH_3	1.28	124	1.28	72
NH_2	1.46	91	1.53	48.5
$N(CH_3)_2$	0.86	109	1.58	30
NO_2	−3.10	0	−4.01	0
SH	−1.55	—	−1.22	135

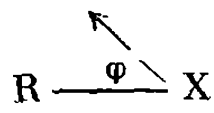
* The positive sign is assigned to the groups X which are the positive poles of the dipole R—X.

** The nonregularity angles φ are found from the dipole moments of the *para*-derivatives of the $X-C_6H_4-Y$ type where Y is a regular substituent which does not interact with X (typically, CH_3 or F, Cl or Br).

—CCl_3, —C≡CH, halogens, etc.) and is at an angle φ to this direction for the nonregular substituents (for instance,



—NH_2, —NR_2, etc):



The same atomic groups can have different dipole moments when they are in molecules of aliphatic or aromatic compounds. For instance, acetonitrile has the dipole moment of $3.47D$ while benzonitrile has the dipole moment of $4.05D$. This difference is caused by the difference between the dipole moments of the bonds C_{sp^3}—H and C_{sp^2}—H, by the difference in hybridization of the carbon atoms linked to the nitrile group, and by other factors which are too involved to be taken into account in full. Therefore, two values of the dipole moment for a group are used, viz. in the aromatic compounds it is the dipole moment of the monosubstituted benzene, and in the aliphatic compounds it is the dipole moment of the monosubstituted methane.

PROBLEMS IN DIPOLE MOMENTS TECHNIQUES

Problem 1. Determine the dipole moments of the disubstituted benzene Cl—C_6H_4—Br using the vector additive scheme.

Answer. From Table 20 we obtain $\mu_{C-Cl} = 1.59D$ and $\mu_{C-Br} = 1.57D$. Eq. (1) yields for the *meta*-position ($\varphi = 120°$, see Fig. 72, *1*):

$$\mu^2_{calc} = \mu^2_{C-Cl} + \mu^2_{C-Br} + 2\mu_{C-Cl}\mu_{C-Br}\cos\varphi =$$

$$= 1.59^2 + 1.57^2 + 2 \cdot 1.59 \cdot 1.57 \cdot (-0.5) = 2.45;$$

$$\mu_{calc} = 1.56D \text{ (to compare: } \mu_{exp} = 1.53D)$$

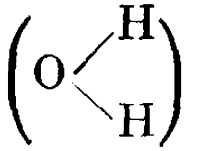
For the *para*-position we obtain ($\varphi = 180°$, see Fig. 72, *2*)

$$\mu_{calc} = 1.59 - 1.57 = 0.02D \qquad (\mu_{exp} = 0.0D)$$

In both cases there is a good agreement between the predicted and measured values.

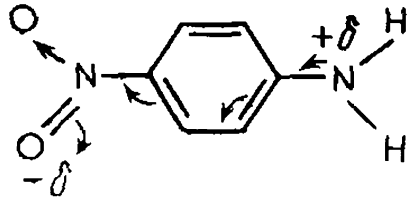
This technique is used, for instance, for determining the molecular geometry (the *cis-trans* forms, *meta-para* positions, valence angles, and so on). To do this, the dipole

moments are calculated for various molecular models by adding the dipole moments of the bonds, and the results are compared with the measured values. The correct structure should have the predicted dipole moment which is the nearest to the measured value.

For instance, the nonzero dipole moments of the molecules H_2O, H_2S, SO_2, $(CH_3)_2O$, etc. confirm that these molecules have the angular  rather than linear (H—O—H) structure where the bonds are at an angle of about 100°.

When a geometric model of a molecule is undoubtedly a correct one but the dipole moment calculated for it differs considerably from the measured value then this difference can yield information on the mutual influence of the bonds and groups in the molecule which has not been taken into account in adding the dipole moments of the bonds.

For instance, the measured dipole moment of *para*-nitroaniline is 6.19*D* and the dipole moment calculated by vector addition is 5.16*D*. The difference between the dipole moments (1.03*D*) is caused by the additional (mesomeric) shift of the electrons



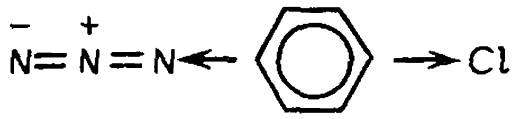
which is specific of this molecule and is not found in the molecules of aniline and nitrobenzene where the dipole moments for the groups NH_2 and NO_2 have been determined.

Problem 2. Find the direction of the dipole moment of the azido group by comparing the measured dipole moment of the *p*-chlorophenylazide (0.3*D*) with the calculated values.

Answer. Using the data of Table 20 calculate the dipole moment of the compound for two possible directions of

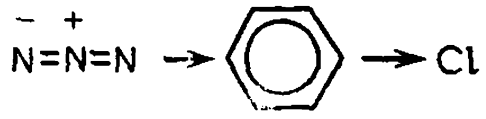
the dipole moment of the azido group:

1.



$\mu_{calc} = 1.59 - 1.44 = 0.15$

2.



$\mu_{calc} = 1.59 + 1.44 = 3.03$

It can be seen that the dipole moment of the azido group should be directed from the ring to the azido group (the structure 1).

Problem 3. Calculate the dipole moments of *m*-dichlorobenzene and *m*-dinitrobenzene using the data of Table 20.

Answer. This problem is similar to Problem 1. The dipole moment of the bond C_{Ar}—Cl is 1.59*D* and that of the bond C_{Ar}—NO_2 is 4.01*D*. It is well-known that in such metadisubstituted benzenes the angle between dipole moments is 120° (cos 120° = —0.5). Eq. (2) yields the following results.

For *meta*-dichlorobenzene: $\mu^2_{calc} = 2\mu_i^2 (1 + \cos \varphi) = 2 \cdot 1.59^2 (1 - 0.5) = 2.51$; $\mu_{calc} = 1.59D$ ($\mu_{exp} = 1.48D$).

For *m*-dinitrobenzene: $\mu^2_{calc} = 2 \cdot 4.01^2 (1 - 0.5) = 16.08$; $\mu_{calc} = 4.01D$ ($\mu_{exp} = 3.90D$).

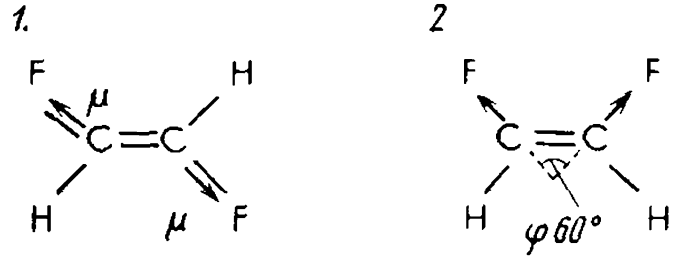
It should be noted that for two identical regular substituents in the *meta*-position ($\varphi = 120°$) the total dipole moment is always equal to the dipole moment of the group (it can be seen from the parallelogram in Fig. 72).

Problem 4. The dipole moment of a lithium fluoride molecule in the gaseous state is 6.67*D* for the internuclear distance $r = 0.152$ nm; for a hydrogen iodide molecule, $\mu = 0.38D$ and $r = 0.162$ nm, and for the hydrogen fluoride molecule, $\mu = 1.97D$ and $r = 0.092$ nm. Determine the ionicities of these molecules. (Here the ionicity is the ratio of the measured dipole moment to the highest possible dipole moment for the molecule.)

Answer. If the bond in the lithium fluoride molecule were fully ionic then the maximum dipole moment of the molecule

with the internuclear spacing of 0.152 nm would be $1.52 \times \times 10^{-8}$ (cm) $\cdot 4.8 \cdot 10^{-10}$ CGSE $= 7.30D$. The measured dipole moment being $6.67D$, the ionicity is $6.67/7.30 = 0.92\%$. Hence, the molecule can be described by the formula Li^+F^- and its bond can be regarded as ionic with a small covalent term (about 8%). The measured dipole moment of hydrogen iodide corresponds to 5% ionicity (0.38/7.80) so that the molecule HI has a normal covalent structure. For hydrogen fluoride the ionicity is 45% (1.97/4.42). Hence, the bond H—F occupies an intermediate position between the purely ionic and purely covalent bonds.

Problem 5. 1,2-Difluoroethylene has *trans*- and *cis*-isomers:



One mixture of isomers has the measured dipole moment of $2.42D$ and another mixture has the dipole moment of $1.7D$. Explain the difference (the dipole moment of the C—F bond is $1.47D$).

Answer. Calculate the dipole moments for both isomers. In the isomer (1) the dipole moments of the C—F bonds have equal magnitudes and opposite directions so that the total dipole moment $\mu_{calc} = 0$. In the *cis*-isomer the angle φ between the dipole moments is 60° and the total dipole moment, according to eq. (2), is $2.55D$. This value is close to the measured dipole moment for the first case indicating that the mixture contained only *cis*-isomer.

The second mixture contains both *trans*- and *cis*-isomers. The contents of the *cis*-isomer is about 70% ($1.7/2.42 \approx 0.7$). When a sample of a symmetric *trans*-isomer shows a nonzero

dipole moment this often indicates an admixture of the *cis*-isomer.

Problem 6. Describe the electronic structure of carbon monoxide CO proceeding from the fact that its dipole moment is 0.11*D*.

Answer. The only electronic structure in which electron octets are both at the oxygen atom and the carbon atom is the structure :C≡O: (one of the bonds is formed by the unshared electron pair of oxygen) in which the atoms have the following charges $:\bar{C}\equiv\overset{+}{O}:$. But this structure should possess a large dipole moment. Another possible electronic structure ($:C=\ddot{O}:$) implies the presence of the normal covalent bond for oxygen but does not provide the complete octet for the carbon atom. This structure ($:\overset{+}{C}=\bar{O}:$) also has a considerable dipole moment but its direction is opposite to that of the first structure.

The charges in these partially ionic bonds are approximately equal. Their mutual compensation accounts for the dipole moment value of CO which seems at first to be anomalously small. Thus, the molecule of CO can be regarded as a resonance hybrid ($:\overset{+}{C}=\bar{O}:$; $:\overset{+}{C}=\bar{\ddot{O}}:$) and cannot be represented by a conventional structural formula.

Problem 7. The dipole moment increases in the compound series CH_3Cl, CH_3CH_2Cl, $(CH_3)_2CHCl$, $(CH_3)_3CCl$ (1.83*D*, 2.03*D*, 2.10*D*, 2.14*D*, respectively). Explain this effect and determine its magnitude.

Answer. The dipole moment increase in the above series of compounds is due to the induction effect. The electronegative chlorine atom causes displacement of electrons from the radicals CH_3, C_2H_5, $(CH_3)_2CH$, and $(CH_3)_3C$, that is, it induces an additional dipole moment in the C—H bonds. With increasing size of the radical the magnitude of the effect drops off and the dipole moment does not increase.

The magnitude of the induction effect can be estimated as the difference between the respective dipole moments:

$$\Delta\mu_{ind} = \mu_{C_2H_5Cl} - \mu_{CH_3Cl} = 2.03D - 1.83D = 0.2D$$

LABORATORY EXERCISES

TECHNIQUES FOR MEASURING DIPOLE MOMENTS

Practically all the techniques used for measuring dipole moments make use of the effect of orientation of molecules in the external electric field. The measurement results are accurate only if orientation of polar molecules is not hindered by some factors, such as association, complexing and other interaction effects. Therefore, measurements are done in gases or vapours under pressures of 20 to 700 mm Hg, or in dilute solutions in nonpolar solvents (benzene, hexane, carbon tetrachloride, dioxane, etc.), at the molar concentrations from 0.2 to 2.0%. In solids, orientation of polar molecules is, typically, rigidly fixed and their dipole moment cannot be measured.

As discussed above the centres of the positive and negative charges in the polar molecules are separated and, hence, the molecules have constant dipole moments, μ_{const}. If an electric field E is applied to the polar molecule this will cause an additional separation r_2 of the electrons and nuclei producing the induced dipole moment μ_{ind} proportional to the electric field:

$$\mu_{ind} = \alpha E$$

where α is the polarizability of the molecule which describes the capacity of the electric charges in the molecule to be displaced by the field.

The total dipole moment is the sum of the constant and the induced dipole moment:

$$\mu = \mu_{const} + \mu_{ind}$$

The induced dipole moment vanishes with removal of the field and it should be distinguished from the constant dipole moment.

Let us consider a small volume V (which contains, however, a large enough number of polar molecules). In the absence of the external electric field the orientations of the dipole moments are random, that is, $\sum \mu_i = 0$.

Denote the dipole moment of a unit volume (1 cm^3) by the vector P referred to as polarization. In the absence of the external field $\sum \mu_i = 0$ and, hence, $P = 0$. The external field tends to align the dipole moments of molecules to the field but the thermal motion of the molecules interferes with this alignment. The polarization under these circumstances known as the orientation polarization is the sum of projections of all the dipole moments in the unit volume on the direction of the external field. Clearly, the total dipole moment of the volume V in non-zero external field is no longer zero. Moreover, the applied field produces the induced dipole moment and, hence, the induced polarization.

The total molecular polarization is the sum of the orientation polarization and the induced polarization:

$$P = P_{\text{orient}} + P_{\text{ind}}$$

The induced polarization depends on the displacements of nuclei and electrons:

$$P_{\text{ind}} = P_{\text{e}} + P_{\text{at}}$$

Then the total polarization is

$$P = P_{\text{orient}} + P_{\text{e}} + P_{\text{at}} \tag{3}$$

Given below is the Debye equation relating the molecular polarization P to the dielectric constant ε and the dipole moment μ of the molecule:

$$P = \frac{\varepsilon - 1}{\varepsilon + 2} \frac{M}{d} = \frac{4}{3} \pi N \left(\alpha + \frac{\mu^2}{3kT} \right) \tag{4}$$

where N is the Avogadro number, k is the Boltzmann constant, T is the absolute temperature, d is the density, and M is the molecular mass.

From the above discussion and eq. (4) we obtain

$$\frac{4}{3}\pi N\alpha = P_{\text{ind}} \tag{5}$$

$$\frac{4}{3}\pi N\frac{\mu^2}{3kT} = P_{\text{orient}} \tag{6}$$

The electronic polarization is approximately equal to the molecular refraction R and can be found from the Lorenz-Lorentz formula:

$$P_e \sim R = \frac{n^2-1}{n^2+2}\cdot\frac{M}{d} \tag{7}$$

where n is the index of refraction.

The dipole moments are calculated from the orientation polarization:

$$P_{\text{orient}} = P - P_e - P_{at}$$

The electronic polarization is found from the molecular refraction by tending the light frequency to zero ($\nu \to 0$, $\lambda \to \infty$). The atomic polarization is estimated using a number of empirical rules (unfortunately, there are no techniques for direct measurement of P_{at}). In most polar compounds P_{at} is negligible compared to P_e and P_{orient}. Therefore, the term P_{at} is, typically, ignored and the molecular refraction is not extrapolated to the zero frequency; the resulting two small errors partially compensate each other and determinations are accurate enough. Thus, the term $P_e + P_{at}$ is taken to be equal to the molecular refraction of the compound for the D line of sodium:

$$P_{\text{orient}} = P - R_D \tag{8}$$

The dipole moment μ can be found from the orientation polarization P_{orient} using eq. (6) which yields, after substi-

tution of the constants,

$$\mu = 0.0128 \sqrt{P_{\text{orient}} T} \tag{9}$$

The molecular polarization is found from the extrapolation equation

$$P = A\left(M_2 - \beta \frac{M_1}{d_1}\right) + \alpha B \tag{10}$$

where A and B are the constants depending on the solvent:

$$A = \frac{\varepsilon_1 - 1}{\varepsilon_1 + 2} \cdot \frac{1}{d_1} \tag{11}$$

$$B = \frac{3M_1}{(\varepsilon_1 + 2)^2 d_1} \tag{12}$$

and M_1 and M_2 are molecular masses of the solvent and the solute, respectively.

The factors α and β are determined graphically (see Fig. 73):

$$\alpha = \left(\frac{\Delta \varepsilon_{12}}{\Delta x_2}\right)_{x_2 \to 0} \tag{13}$$

$$\beta = \left(\frac{\Delta d_{12}}{\Delta x_2}\right)_{x_2 \to 0} \tag{14}$$

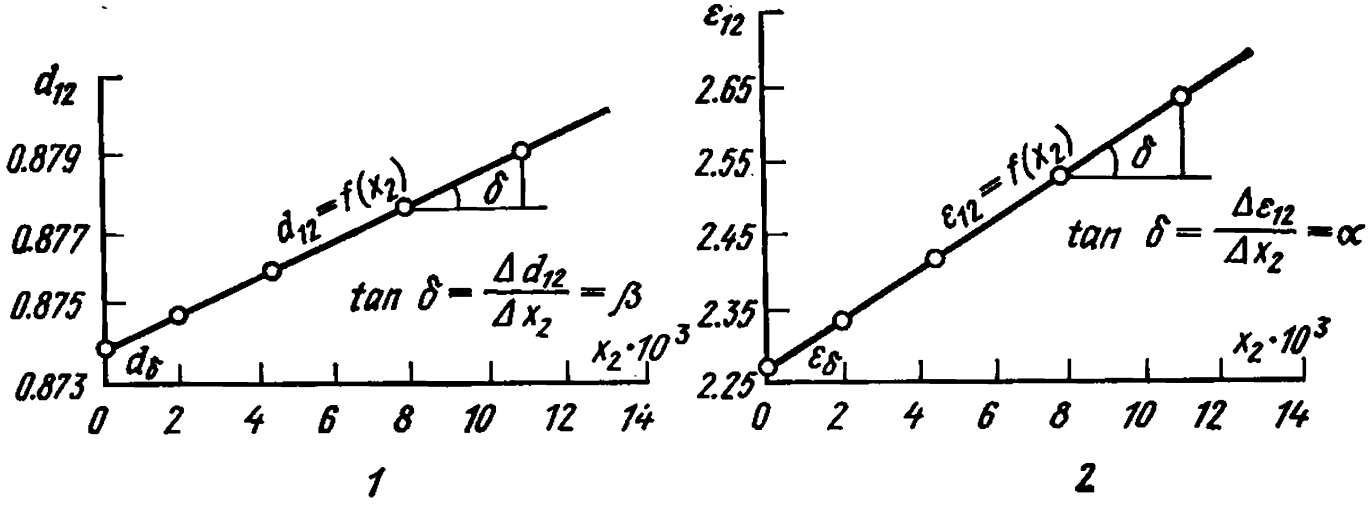


Fig. 73.
Graphical determination of the factors β (*1*) and α (*2*) in eq. (10). Plots represent the values of the parameters d_{12}, x_2, ε_{12} measured for β-nitrostyrene in benzene which are close to the real values (1 mm on the x_2 axis is $2 \cdot 10^{-5}$; 1 mm on the ε_{12} axis is 10^{-3}; 1 mm on the d_{12} axis is $2 \cdot 10^{-5}$ g/cm^3).

Exercise 1. Measurement of Molecular Refraction

The molecular refraction is to be determined for solids and liquids by using experimental and computation techniques.

Determination of the molecular refraction is a necessary step in calculation of the dipole moments. As shown above, the sum $P_e + P_{at}$ in eq. (8) can be replaced by the refraction R_D. If the molecules of the compound under study have no conjugated bonds the refraction can be calculated with a satisfactory accuracy by adding the atomic refractions which can be taken from the handbooks. For liquids the refraction R_D can be found experimentally by measuring the index of refraction and the density of the pure compound. For solids the molecular refraction is found from measurements of R_D and d, for a series of solutions.

Operational procedure:

(1) Measure (for benzene, nitrobenzene and ethanol) the index of refraction (using a refractometer) and density by the gravimetric technique. The samples should be thermostatted at 25° C. Repeat the measurements 3-4 times and calculate the mean values to four decimals.

(2) Prepare dilute solutions (be sure to record separately the weights of the solvent and the solute), for instance, the benzene solutions of β-nitrostyrene and naphthalene (or other solutions) and carry out measurements as in step 1.

(3) Calculate the refraction R_D for the liquids using eq. (7) and then using the known atomic refractions and bond increments (which can be found in chemical handbooks). For instance, for C_2H_5OH calculations yield: $2C + 6H + O = 2 \cdot 2.418 + 6 \cdot 1.1 + 1.525 = 12.961$. Compare the measured and calculated values.

(4) For solids the refraction R_2 is found using the following

equations:

$$R_{1,2} = \frac{n_{1,2}^2 - 1}{n_{1,2}^2 + 2} \frac{M_1 x_1 + M_2 x_2}{d_{1,2}} \tag{15}$$

$$R_2 = \frac{R_{1,2} - R_1}{x_2} + R_1 \tag{16}$$

where $n_{1,2}$, $d_{1,2}$ and $R_{1,2}$ are, respectively, the index of refraction, the density, and the molecular refraction of the solution; R_1 is the molecular refraction of the solvent (found in step 1), M_1 and M_2 are the molecular masses of the solvent and the solute, x_1 and x_2 are their molar fractions

$$x_2 = \frac{q_2/M_2}{q_2/M_2 + q_1/M_1} \tag{17}$$

where q_1 and q_2 are the weights of the solvent and the solute ($x_1 = 1 - x_2$).

Calculate R_2 from the atomic refractions and compare the results.

Exercise 2. Measurement of Dipole Moments

Dipole moments will be found from measurements of the dielectric constant and the density of dilute solutions. Any equipment can be used provided the accuracy of measurements is high enough. In the instruments based on the beat technique the measurement cell is filled with the solution which changes the capacitance of the cell. This change is compensated by a calibrated precision capacitor. The difference signal is amplified and measured. The measurement error for the dipole moment of $4D$ is about $0.02D$.

Operational procedure:

(1) Purify the solvent which should satisfy the requirements for dielectric measurements. Prepare 5-7 solutions of nitrostyrene in benzene (x_2 varies from $0.2 \cdot 10^{-2}$ to 10^{-2}), record the weights q_1 (about 50 g) and q_2 (from 100 to 600 mg)

to 0.1 mg and measure the dielectric constant of the pure solvent at 25° C. Determine the density of the solutions.

(2) Measure the dielectric constants of the prepared solutions.

(3) Tabulate the experimental results (see Table 21).

TABLE 21

EXPERIMENTALLY OBTAINED DIPOLE MOMENTS OF β-NITROSTYRENE

Solution	q_2 (g)	q_1 (g)	$10^3 x_2$	d_{12} (g/cm^3)	ε_{12}
Solvent	—	42.1437	—	0.8737	2.2725
Solution 1	0.1656	42.1437	2.086	0.8747	2.3437
Solution 2					
Solution 3					
Solution 4					
Solution 5					

(4) Table 21 illustrates the procedure by giving the data for the pure solvent and one nitrostyrene solution. Nitrostyrene has the formula $C_6H_5—CH=CHNO_2$, $M_2 = 149$; the standard nonpolar solution is benzene, $M_1 = 78$. Hence,

$$x_2^1 = \frac{0.1656/149}{0.1656/149 + 42.1437/78} = 2.086 \cdot 10^{-3} \text{ (see eq. (17))}$$

(5) Calculate x_2 values for all solutions according to step 4 and plot the functions $\varepsilon_{12} = f(x_2)$ and $d = f(x_2)$ (see Fig. 73). Find the factors α and β, i.e. the slopes of the plots.

(6) Calculate the molecular refraction (see Exercise 1).

(7) Calculate P, P_{orient} and the dipole moment μ using eqs. (10), (8) and (9).

(8) Compare the result with the reported value.

Note. Nitrostyrene may be replaced by another compound but it should have a large dipole moment.

Exercise 3. Determination of the Dipole Moments of the Isomeric (*o*-, *m*- and *p*-) Dichlorobenzenes (or Dinitrochlorobenzenes)

Operational procedure:

(1) Determine the dipole moment μ_{exp} of an isomer (with unknown positions of the substituents) as in Exercises 1 and 2.

(2) Calculate the dipole moments for various isomers, and determine the structure of the isomer. Calculate the error of determination of the dipole moment using the reported value μ_{rep} of the dipole moment:

$$\frac{\mu_{exp} - \mu_{rep}}{\mu_{rep}} \cdot 100\%$$

(3) Calculate the dipole moment of the chlorine-carbon bond using the measured dipole moment, and determine the error as in step 2 (make use of Table 20).

PROBLEMS INVOLVING IR, RAMAN, UV AND NMR SPECTROSCOPY

Problem 1. Gas-liquid chromatography of the products of the reaction between *tert*-pentylbromide and a water-80%-ethanol mixture indicates formation of three compounds which produce three peaks different from the peaks of the reactants and solvents (different retention times). The relative amounts of the products were determined using the internal standard: compound (1)—60%, compound (2)—32% and compound (3)—8%. After separation of the products they were analyzed and the following data were obtained.

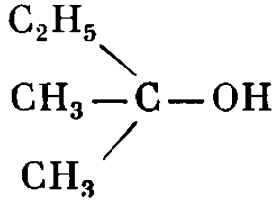
1. The molecular mass — 88. The IR spectrum has a high-intensity narrow band at about 3600 cm^{-1} (for highly diluted

solution) and bands at about 2960 and 2860 cm^{-1}, 1385, 1360 and 1160 cm^{-1}.

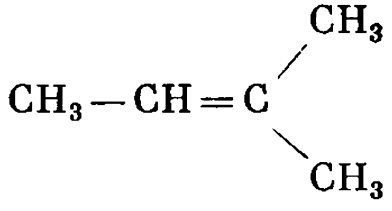
2. The molecular mass—70. The IR spectrum has a weak band at 1670 cm^{-1}, a doublet at 1380 and 1360 cm^{-1}, and high-frequency bands at 2960 and about 2870 cm^{-1}. The NMR spectrum has a singlet with $\delta = 1.7$ ppm and a quartet with $\delta = 5.0$ ppm.

3. The molecular mass—70. The IR spectrum has a high-intensity band at 1650 cm^{-1}. The NMR spectrum has a signal with $\delta = 5.3$ ppm and a singlet with $\delta = 1.7$ ppm.

Answer. 1. The molecular mass and the IR spectrum suggest the presence of the tertiary hydroxyl group ($\nu_{OH} = 3600$ cm^{-1} and $\nu \approx 1160$ cm^{-1}), methyl and methylene groups. The compound may be a tertiary alcohol of the following structure:

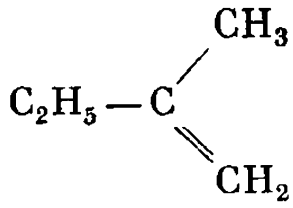


2. The absorption bands at 1670, 1380 and 1360 cm^{-1} can evidence the presence of the double bond and the *hem*-dimethyl group, respectively. The absorption bands at 2960 and about 2870 cm^{-1} are also due to vibrations of the CH bonds. In the NMR spectrum the singlet with $\delta = 1.7$ ppm indicates the presence of two methyl groups at the double bond while the quartet is due to the proton at the double bond. Hence, the compound can have the structure of the trisubstituted alkene:



3. The high-intensity band at 1650 cm^{-1} suggests the presence of the double bond. The signal with $\delta = 5.3$ ppm

is due to the protons of the vinyl group $=CH_2$ and the singlet with $\delta = 1.7$ ppm is due to the methyl group at the double bond. Hence, the following structure can be suggested:



Problem 2. A compound dissolved in heptane has a UV absorption peak at 275 nm ($\varepsilon_{max} = 14.5$).

1. What is the origin of this band if in the methanol solution its peak is at 271.5 nm?
2. What is the structure of the compound if it has high-intensity IR bands at 1578 and 1390 cm^{-1} and a single peak with $\delta = 4.27$ ppm in the NMR spectrum?
3. What should be the effect of replacement of the nonfunctional group with phenyl on the intensity and position of the UV band?

Answer. 1. The low intensity of the UV band suggests that the transition is a forbidden one. The position of the absorption peak and the effect of the solvent show that this is an $n \rightarrow \pi^*$ transition (examples are transitions in carbonyl, nitro, nitroso, thiocarbonyl and other groups).

2. The high-intensity IR bands at 1390 and 1578 cm^{-1} are due to the symmetric and asymmetric stretching vibrations of the nitro group, respectively. The fact that there is a single NMR signal and the value of its chemical shift suggest that the nitro group is a neighbour of the methyl group. Thus, the compound is nitromethane, CH_3NO_2.

3. The bathochromic effect should be expected for the $n \rightarrow \pi^*$ transition in nitrobenzene. The effect is due to conjugation between the NO_2 group and the benzene ring.

Problem 3. The IR spectrum of the pure propionic acid has a high-intensity wide band with a diffuse peak at about 3000 cm^{-1} and two bands of considerably smaller widths at

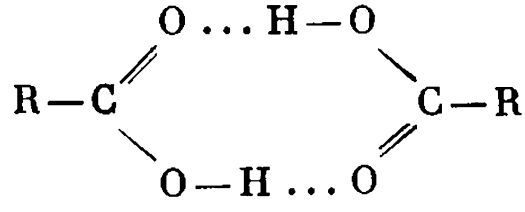
1758 and 1710 cm^{-1}. The band at 1758 cm^{-1} is a shoulder of the band at 1710 cm^{-1} which has a very high intensity. The ratio of intensities of these two bands varies upon dilution with a nonpolar solvent.

1. Estimate the effect of decreasing concentration on the ratio of the intensities of these bands in carbon tetrachloride.

2. If carbon tetrachloride is replaced with dioxane the two bands merge into the band at 1735 cm^{-1}. Explain this phenomenon. What other solvents can produce the same effect?

3. The NMR spectrum of the carbon tetrachloride solution of propionic acid has only one signal of the hydroxyl proton with the chemical shift of about 11 ppm. Explain the difference between the IR and NMR spectra.

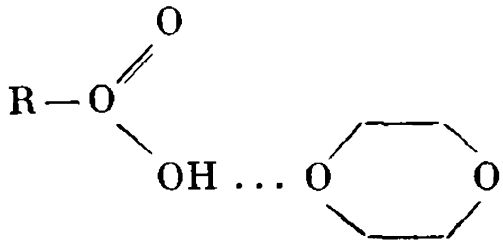
Answer. 1. The IR spectra of acids have a very wide diffuse characteristic band at 3000 cm^{-1} which is attributed to strong association due to hydrogen bonding. This can be seen from the comparison of the position of the band for the bound OH group with the positions of the bands for the free and bound OH groups in alcohols (about 3600 and 3300 cm^{-1}, respectively). This strong association can be explained by formation of the dimer



Under such circumstances the two $\nu_{C=O}$ bands at 1758 and 1710 cm^{-1} can be assigned to the monomer and dimer, respectively. If the acid is pure the latter band has a much higher frequency than the former one. This is confirmed by variation of the relative intensity of the bands with dilution in a nonpolar solvent since one of the bands is due to the free OH group and the other one to the bound group.

Dilution in carbon tetrachloride reduces intermolecular association and increases the intensity of the monomer band $\nu_{C=O}$ at 1758 cm^{-1} and decreases the intensity of the dimer band $\nu_{C=O}$ at 1710 cm^{-1}. The content of the dimer molecules decreases while the content of the monomer molecule increases.

2. Dilution with dioxane also decreases the number of the dimer molecules but, instead of the free acid molecules the solvated molecules are formed for which the frequency $\nu_{C=O}$ is higher than that for the free molecules but lower than for dimer molecules whose degree of association is much higher:



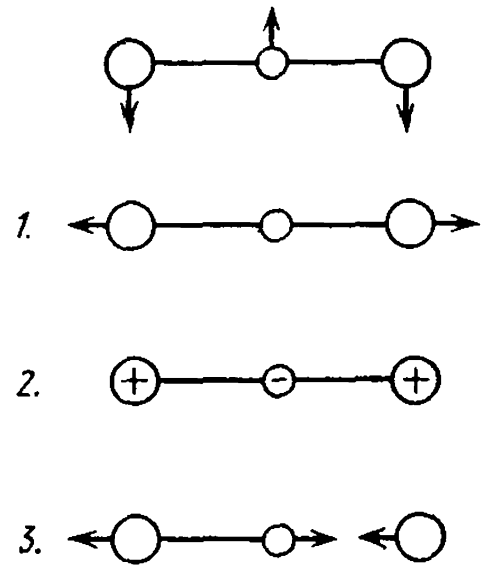
Such solvation can occur in any oxygen-containing basic solvent and it is the higher the higher the basicity of the solvent (for instance, esters, and in particular, tetrahydrofuran).

3. Acid monomer and dimer in carbon tetrachloride cannot be distinguished in the NMR spectrum as they give one signal. The lifetimes of molecules in the free and bound states are long enough to produce separate bands in the IR spectrum but too short to give separate NMR signals.

The "exposure time" in NMR spectroscopy is too long (owing to relaxation) to record several hydroxyl signals for each state of the acid molecule and therefore an "averaged" signal is recorded.

Problem 4. Classify the following molecules according to the characteristics of the IR and Raman spectra: (1) Cl_2, (2) HCl, (3) CO, (4) $CF_2=CH_2$ (only the stretching vibrations of the double bond), (5) $CH_3CH=CHCH_3$ (only the stretching vibrations of the double bond).

Fig. 74.
Vibrations in the CO_2 molecule: *1*—symmetric stretching vibration of C=O (ν_1); *2*—deformation (degenerate) vibration of OCO (ν_2); *3*—asymmetric stretching vibration of C=O (ν_3).



Answer. 1. The molecule Cl_2 shows no IR activity and has high-intensity Raman lines.

2. The molecule HCl is both IR- and Raman-active.

3. The molecule CO is IR active ($A = 0.53 \cdot 10^4$ red. units).

4. In the molecule $CF_2{=}CH_2$ the double bond is IR active and has low Raman activity.

5. In the molecule $CH_3CH{=}CHCH_3$ the double bond has no IR activity and has a very high-intensity line in the Raman spectrum.

Problem 5. Carbon dioxide has two IR absorption bands but only one Raman line; all of them are associated with different vibrations. Determine three different types of atom vibrations for the molecule O=C=O which do not displace its centre of gravity. Find which vibrations are IR active, that is, make the molecule electrically asymmetric (for a fraction of the vibration period) and which vibration is Raman active, that is, does not violate the electric symmetry of the molecule.

Answer. Carbon dioxide has zero total dipole moment (Fig. 74, Table 22). Table 23 gives the main vibrational frequencies and intensities for CO_2.

TABLE 22

Band characteristic	ν_1	ν_2	ν_3
Dipole moment variation	0	Perpendicular to the axis	Parallel to the axis
Polarizability variation	Nonzero	0	0
Activity	In Raman spectrum	In IR spectrum	In IR spectrum

TABLE 23

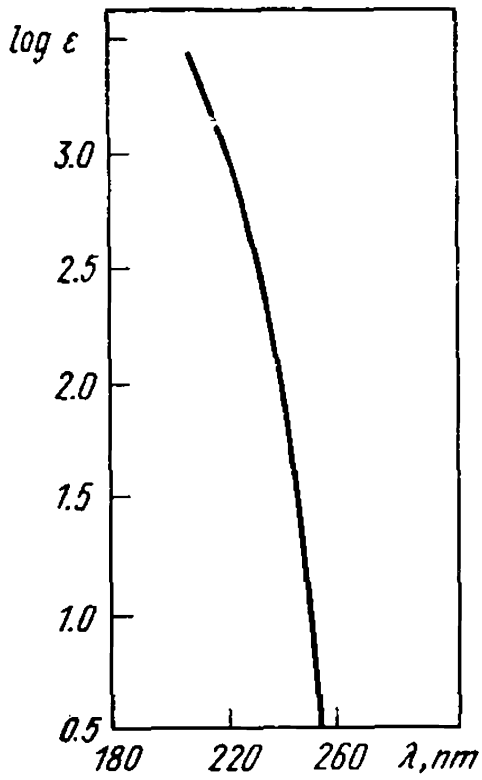
THE MAIN VIBRATIONAL FREQUENCIES FOR THE CO_2 MOLECULE

Vibration type	Frequency (cm^{-1})	IR band intensity ($A \cdot 10^{-4}$ $l \cdot mole^{-1} \cdot cm^{-2}$)
Symmetric stretching vibrations of the C=O bond (ν_1)	1345	0
Deformation vibrations of OCO (ν_2)	667	0.54
Antisymmetric stretching vibrations of the C=O bond (ν_3)	2349	6.03

Problem 6. Explain the UV, IR and NMR spectra of vinyl acetate $CH_2 = CHOOCCH_3$ given in Figs. 75, 76, 77.

Answer. The IR spectrum shows the presence of the carbonyl group ($\nu_{C=O} = 1760$ cm^{-1}) and the double bond ($\nu_{C=C} = 1645$ cm^{-1}). The bands at 1430 and 1370 cm^{-1}, and 980, 950 and 870 cm^{-1} are assigned to the deformation vibrations of the methyl and methine groups. In the NMR spectrum the singlet with $\delta = 2.12$ ppm is produced by the protons of the methyl group near the carbonyl group. The

Fig. 75.



methylene protons of the vinyl group produce a multiplet (δ = 4.5-5 ppm). The ester group affects shielding of the methine proton, shifting its signal upfield (δ = 7.22). The UV absorption is due to the ester group.

Problem 7. Explain the UV, IR and NMR spectra of N,N-dimethylacetamide given in Figs. 78, 79 and 80.

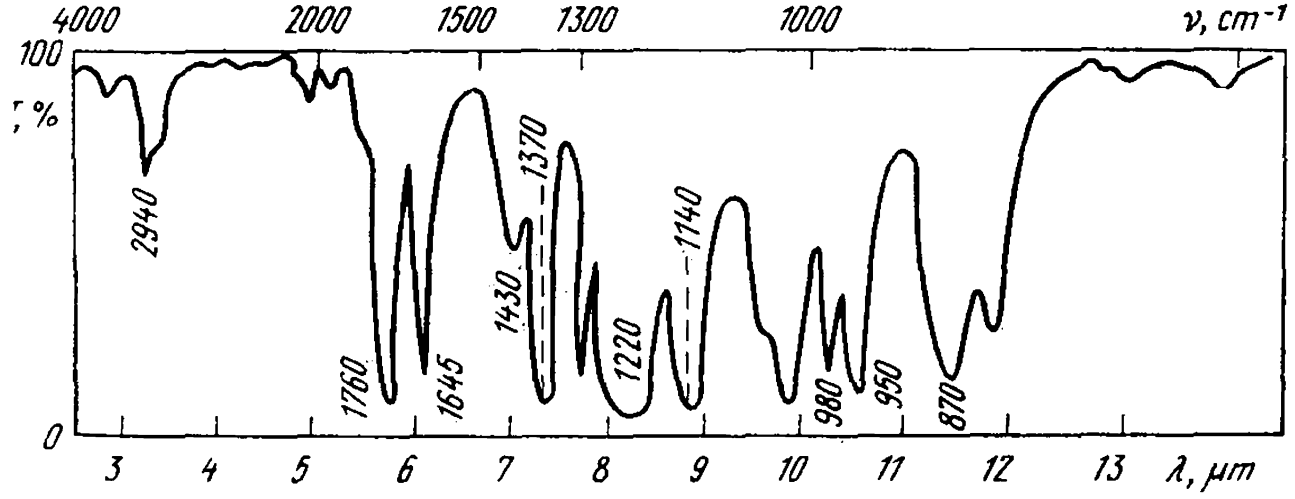


Fig. 76.

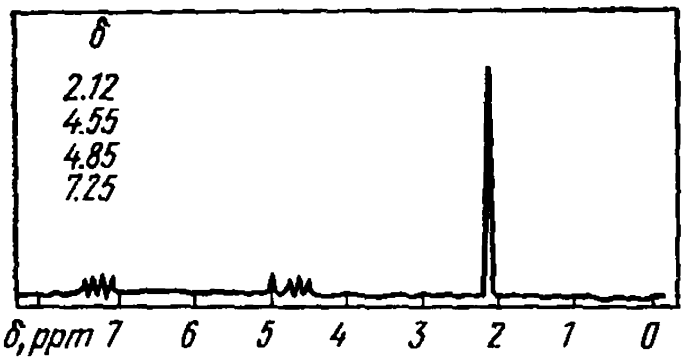


Fig. 77.

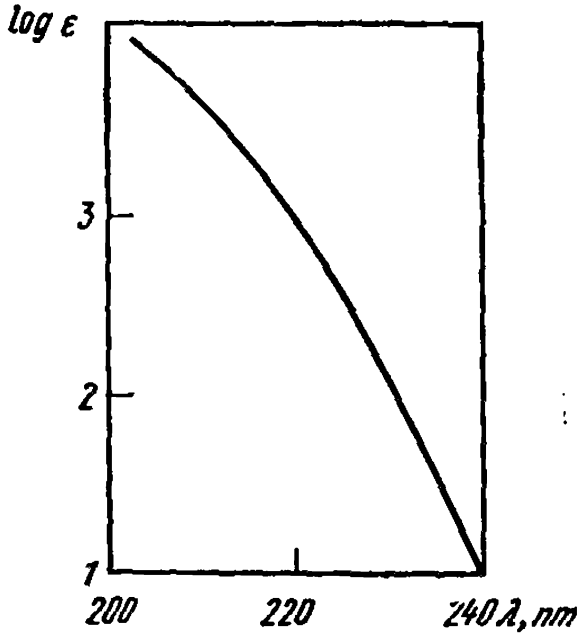


Fig. 78.

Answer. The high-intensity IR band at 1650 cm^{-1} can be assigned to the carbonyl group. The low-frequency $\nu_{C=O}$ is characteristic for amides. The band at 2940 cm^{-1} indicates the presence of the methyl group.

In the NMR spectrum the singlet with $\delta = 2.08$ ppm should be assigned to the protons of the acetyl group, CH_3CO. Owing to the asymmetry of the dimethylacetamide molecule the methyl protons at the nitrogen atom are not equivalent

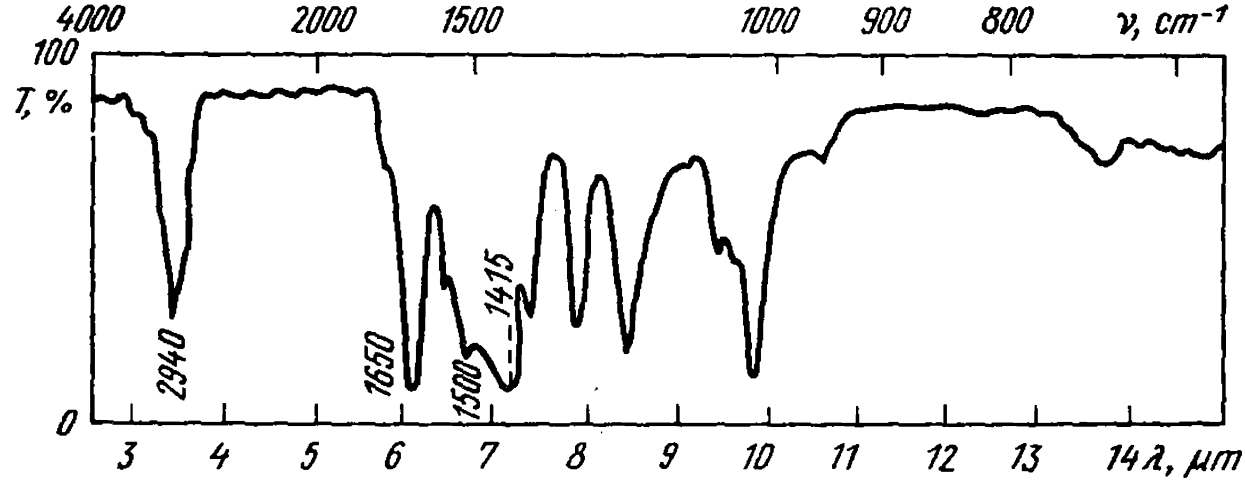


Fig. 79.

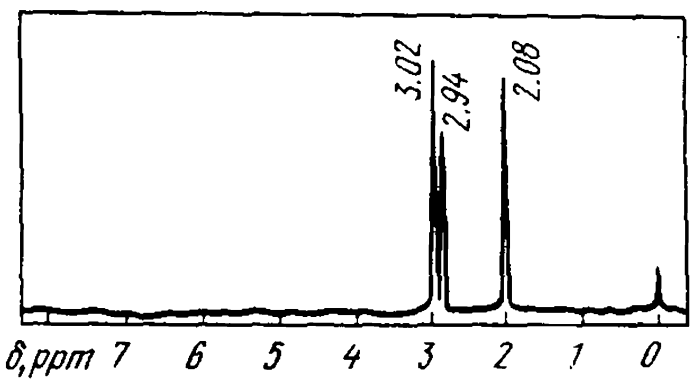


Fig. 80.

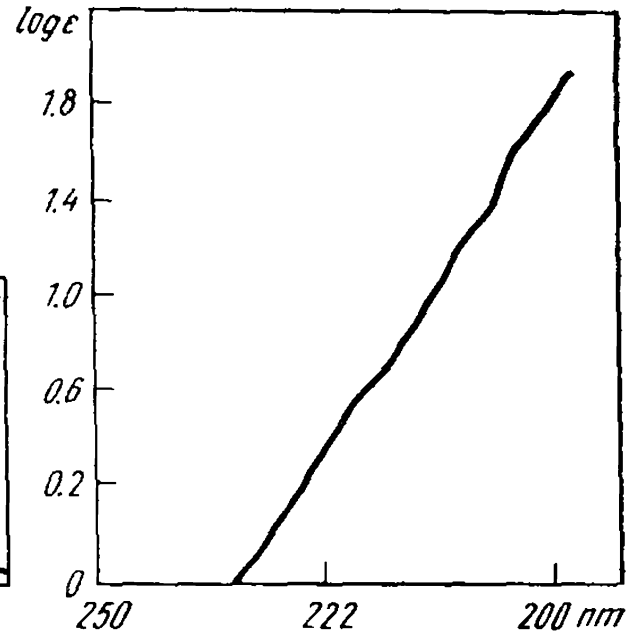
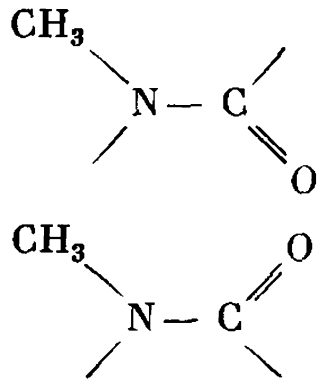


Fig. 81.

and should have different chemical shifts:



2.94 ppm

3.02 ppm

The UV absorption should be assigned to the amide group.

Problem 8. The UV, IR and NMR spectra of the compound $C_4H_7N_2$ are given in Figs. 81, 82 and 83. Determine the structure of the compound.

Answer. The high-intensity band at 2960 cm^{-1} and the band at 1460 cm^{-1} show the presence of the methine group. The band at 2230 cm^{-1} is due to vibration of the nitrile group and the doublet at 1390 and 1370 cm^{-1} is characteristic for the *hem*-dimethyl group. Thus, the logical structure to suggest is $(CH_3)_2NCHCN$.

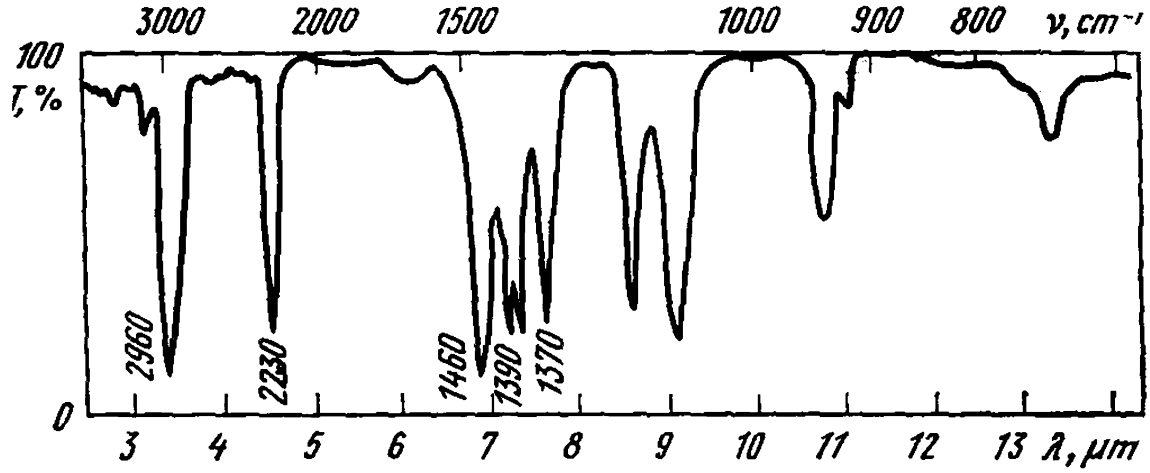


Fig. 82.

The NMR spectrum confirms this structure. The doublet with $\delta = 1.33$ ppm (6 H) shows that two equivalent methyl groups are located close to the methine proton (see the multiplicity rule). The multiplet with $\delta = 2.72$ ppm (1H) is given by the methine proton.

Problem 9. The compound C_4H_7ON has no absorption peaks in the UV spectrum. Its IR and NMR spectra are shown in Figs. 84 and 85. Determine the structure of this compound.

Answer. The IR spectrum suggests that the compound contains methyl and methylene groups (the stretching and deformation bands of the C—H bonds at 2870, 1465, 1420 and 1385 cm^{-1}) and the nitrile group ($\nu_{CN} = 2220$ cm^{-1}). In the NMR spectrum the singlet with $\delta = 3.4$ ppm is characteristic for the protons of the methyl group neighbouring with the oxygen atom, and two triplets (3.62 and

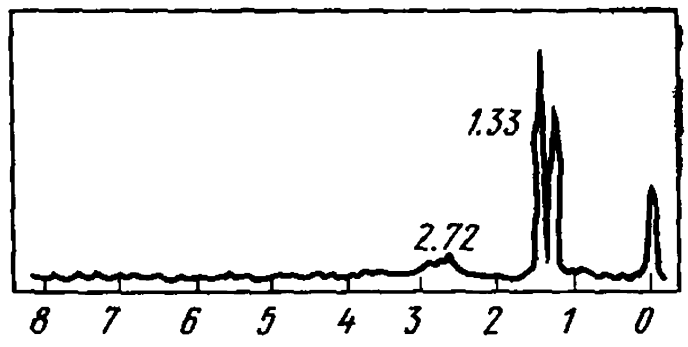


Fig. 83.

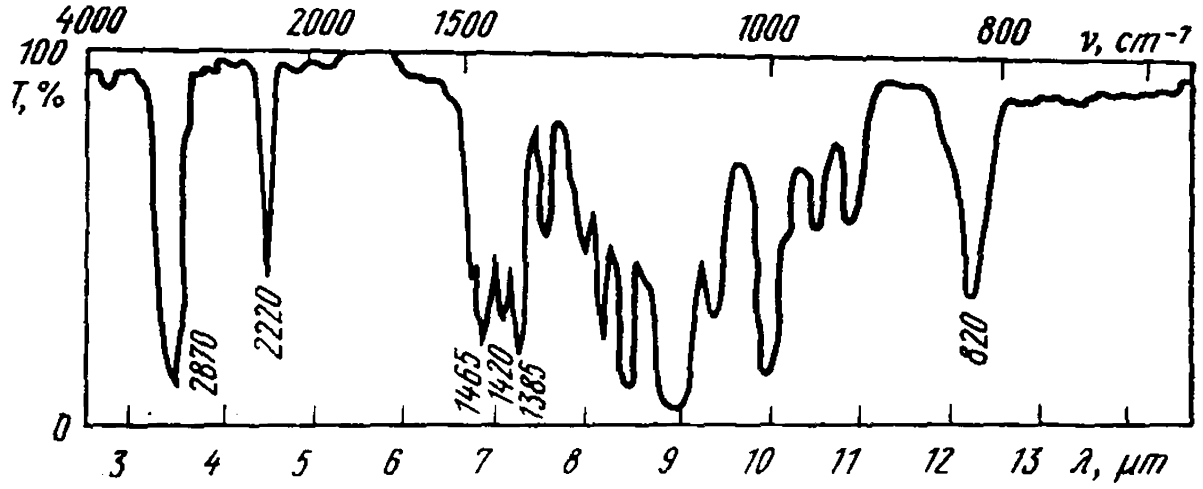


Fig. 84.

2.62 ppm) are given by the methylene groups at the oxygen atom and the nitrile group, respectively. Hence, the compound can be identified as $CH_3OCH_2CH_2CN$.

Problem 10. The solid compound $C_8H_4N_2$ has the following spectral features: NMR singlet with $\delta = 7.8$ ppm; IR bands at 3100 (w.), 2240 (s.), 1600 (w.), 1570 (w.), 1495 (m.), 1450 (w.), 1300 (w.), 1200 (w.), 960 (w.), and 770 (s.) cm^{-1}; and UV bands (in ethanol) at 283 and 292 nm ($\varepsilon = 1600$ and 1820); UV absorption of higher intensity is found below 240 nm. Determine the structure of the compound.

Answer. The spectroscopic data should be analyzed in the region of absorption by functional groups. The strong band at 2230 cm^{-1} may suggest the nitrile group. The empirical formula implies the presence of two nitrile groups. A number of bands (at 3100, 1600, 1570 and 1495 cm^{-1}) are due to the aromatic ring. The NMR spectrum confirms this since

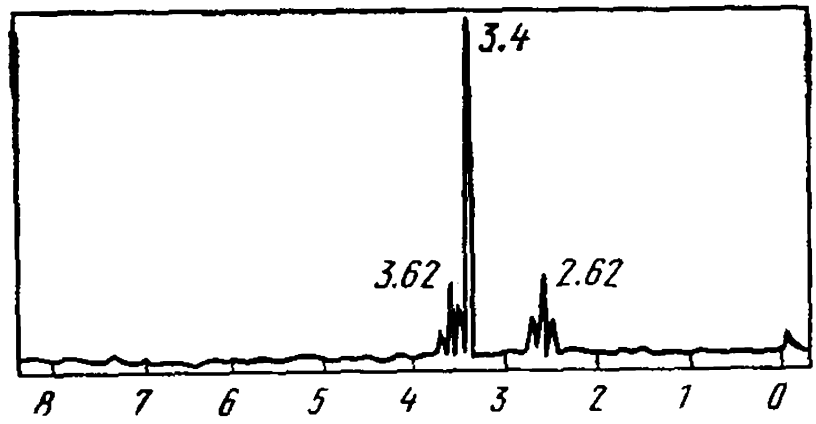
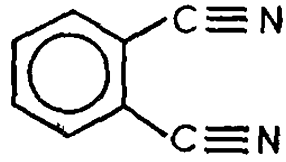


Fig. 85.

the signal with $\delta = 7.8$ ppm is typical for the aromatic protons. The positions of substituents can be determined from the IR spectrum. The strong band at 770 cm^{-1} can indicate the presence of two *ortho*-substituents. In the UV spectrum the high-intensity absorption peaks at 283 and 292 nm suggest a conjugated system. Thus, the structure suggested for the compound is



Problem 11. A lachrimatory liquid $C_4H_4Cl_2$ has the following spectral features: NMR line (in CCl_4) with $\delta = 4.2$ ppm; and IR bands at ~2960 (w.), 1430 (m.), 1265 (v. s.), 1165 (s.) and 710 (v. s.) cm^{-1}. Determine the structure of the compound.

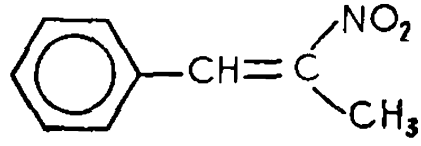
Answer. The IR spectrum of the compound is rather simple owing to the high symmetry of the molecule. Three high-intensity bands at 1265, 1165 and 710 cm^{-1} are due to vibrations of the CH_2—Cl groups. The empirical formula implies a triple bond. The lack of a band $\nu_{C\equiv C}$ in the IR spectrum is also attributed to the symmetry of the molecule (these vibrations should be active in the Raman spectrum). In the NMR spectrum the singlet with $\delta = 4.2$ ppm evidences separation of the chloromethyl groups. Hence, the compound's structure is $ClCH_2C{\equiv}CCH_2$—Cl.

Problem 12. A compound has the empirical formula $C_9H_9NO_2$. Its Raman spectrum has high-intensity bands at 1600, 1640 and 1335 cm^{-1}. The IR spectrum has the bands at 1655 (m.), 1528 (s.) and 1318 (v. s.) cm^{-1}. The NMR spectrum has three singlets with the intensity ratio of 5 : 3 : 1. The signal of the highest intensity has $\delta \approx 7$ ppm. Determine the structure of the compound.

Answer. A comparison of the IR and Raman spectra suggests the presence of the nitro group and the double bond. In the IR spectrum the high-intensity bands at 1528 and

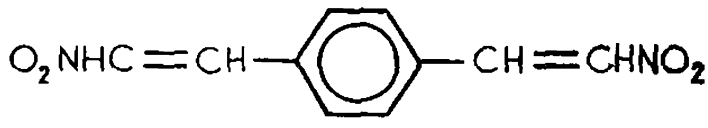
1318 cm^{-1} are associated with vibrations of the conjugated nitro group. The low frequency ν_s for the nitro group is noteworthy as it is, typically, associated with the steric effect.

The Raman spectrum has a band of symmetric stretching vibration of the nitro group (1335 cm^{-1}). The bands at 1655 (IR) and 1640 cm^{-1} (Raman) should be assigned to vibrations of the double bond. The high-intensity Raman band at 1600 cm^{-1} indicates the aromatic ring. The chemical shift value and the NMR intensity ratio suggest that the signal with the highest intensity is given by the phenyl protons. The lack of signal splitting (3 H) shows the absence of the spin-spin coupling for the methyl group; hence, there are no protons at the neighbouring carbon atom. Thus, the compound can be assigned the structure of the α-substituted nitrostyrene:



Problem 13. A compound has the empirical formula $C_{10}H_8N_2O_4$. Its Raman spectrum has the high-intensity bands at 1610, 1625, 1510 and 1335 cm^{-1}; the IR bands are at 1616 (w.), 1540 (s.), 1320 (s.) and 940 (m.); the UV spectrum has $\lambda_{max} = 310$ nm and $\varepsilon = 22\,320$. Determine the structure of the compound.

Answer. The Raman bands at 1610 and 1625 cm^{-1}, characteristic of the double bond and the benzene ring, show that the molecule is symmetric. A comparison of the IR and Raman data indicates the presence of the nitro group. The empirical formula implies two nitro groups. In the UV spectrum the high values of λ_{max} and ε_{max} are explained in terms of absorption by the benzene ring conjugated with the π-electrons of the double bond. Thus, the structure of the compound is



Problem 14. A compound has the structural formula $CH_3CH_2C(=O)CH_2CH_3$. Describe the IR, UV and NMR spectra of this compound.

Answer. The IR spectrum of the compound should contain a band associated with vibrations of the alkyl CH groups ($\sim 2970\,cm^{-1}$) and a high-intensity carbonyl band ($\sim 1720\,cm^{-1}$). The UV spectrum should have a low-intensity absorption peak at 270 nm. The NMR spectrum should contain a characteristic triplet ($\delta_{CH_3} \approx 1$ ppm) and a quartet ($\delta_{CH_2} \approx \approx 2.4$ ppm) indicative of the ethyl group.

Problem 15. A compound has the empirical formula $C_5H_8O_3$. The IR spectrum has the bands at 3300 cm^{-1} (wide), 2300 cm^{-1} and 1715 cm^{-1} (wide). The UV spectrum has a low-intensity band at 262 nm, and the NMR spectrum contains a signal at 11.0 ppm, a high-intensity singlet at 2.12 ppm, and a triplet at 2.60 ppm. Identify the compound.

Answer. The IR spectrum of the compound corresponds to a carboxylic acid. The wide band at 3300 cm^{-1} and the band at 2300 cm^{-1} are associated with the stretching vibration of the bound OH group, and the strong band at 1715 cm^{-1} is characteristic of the carbonyl group of the aliphatic carboxylic acid. The proton of carboxylic acid gives the NMR signal at 11.0 ppm. The high-intensity singlet at 2.12 ppm is given by the CH_3 group at the ketone carbonyl group. The triplet at 2.60 ppm is associated with two methylene groups which have almost identical chemical shifts under the effect of the carbonyl and carboxyl groups. The low-intensity UV band at 262 nm indicates the presence of the unconjugated keto group. The compound may have the following structure: $CH_3C(=O)CH_2CH_2COOH$.

Appendix

TABLE 1a

CHARACTERISTIC FREQUENCIES FOR VARIOUS ATOMIC GROUPS IN THE IR REGION

Compound	Frequency (cm^{-1})	Intensity* (ε)	Notes
A. Hydrocarbons			
Alkanes	2975-2950	s.-m. (70)	ν_{asCH_3}
	2885-2860	m.	ν_{sCH_3}
	1470-1430	m.	δ_{asCH_3}
	1385-1370	s.	δ_{sCH_3}
	~ 1340	w.	δ_{CH}, practically unused
	1485-1445	m.	δ_{CH_2}, scissors
	1395-1380	s.	*hem*-dimethyl
	1370-1365	s.	
	1395-1385	**m.**	*tert*-butyl
	~ 1365	s.	
Alkenes			
mono-substituted	3095-3010	m.	ν_{asCH_2}
	2975	m.	ν_{sCH_2}
	3040-3010	m.	ν_{CH}
	1680-1620	var. (40)	$\nu_{C=C}$
	1420-1410	m. (10)-(20)	δ_{CH_2} in-plane
	995-985	s. (50)	δ_{CH} out-of-plane

* Abbreviations: s.—strong, m.—medium, w.—weak, wide, var.—variable, n—narrow, b—broad.

Table 1a, continued

Compound	Frequency (cm^{-1})	Intensity* (ε)	Notes
	915-905	s. (110)	δ_{CH_2} out-of-plane
disubstituted			
cis-	3040-3010	m.	ν_{CH}
	1665-1635	m. (10)	$\nu_{C=C}$
	690	s. (40)	δ_{CH} out-of-plane
trans-	3040-3010	m.	ν_{CH}
	1675-1665	w. (2)	$\nu_{C=C}$
	1310-1295	m.	δ_{CH} in-plane
	970-960	s. (100)	δ_{CH} out-of-plane
hem-	3095-3075	m.	ν_{CH_2}
	~ 1655	m. (35)	$\nu_{C=C}$
	1420-1410	s.	δ_{CH_2} in-plane
	895-885	s. (100)	δ_{CH_2} out-of-plane
trisubstituted	3040-3010	m.	ν_{CH}
	~ 1670	m.	$\nu_{C=C}$
	840-790	s. (40)	δ_{CH} out-of-plane
tetrasubstituted	1690-1670	w.	$\nu_{C=C}$
conjugated (dienes)	1650, 1600	w.	$\nu_{C=C}$
conjugated with phenyl	~ 1625	s.	$\nu_{C=C}$
conjugated with the C=O group	1660-1580	s.	$\nu_{C=C}$
Alkynes			
monosubstituted	3300	s. (100)	ν_{CH}
	2140-2100	w. (5)	$\nu_{C\equiv C}$
	630	s.	δ_{CH}
disubstituted	2260-2190	var., w.	$\nu_{C\equiv C}$, not found for symmetry
Allenes	1970-1950	m.	Splits for end position and at addition to electron-acceptor groups
	1060	m.	
	850	m.	δ_{CH}, found only at end position

Table 1a, continued

Compound	Frequency (cm^{-1})	Intensity* (ε)	Notes
Aromatic compounds	3080-3030	var. (60)	ν_{CH}, typically several bands
	~ 1600	var.	Vibrations of aromatic ring
	~ 1580	var.	
	~ 1500	m.	
	~ 1450	m.	
Substitution type*			
5 neighbouring atoms H	~ 750	var., s.	Out-of-plane deformation vibrations of CH
	~ 700	var., s.	
4 neighbouring atoms H	~ 750	var., s.	
3 neighbouring atoms H	~ 780	var., m.	
2 neighbouring atoms H	~ 830	var., m.	
1 atom H	~ 800	var., m.	
B. Oxygen-containing compounds			
Ketones			
saturated acyclic	1725-1705	s. (300-600)	$\nu_{C=O}$
saturated cyclic			
6-member or more	1725-1705	s.	$\nu_{C=O}$
5-member	1750-1740	s.	$\nu_{C=O}$
4-member	1775	s.	$\nu_{C=O}$
α, β-unsaturated acyclic	1685-1665	s.	$\nu_{C=O}$
α, β-unsaturated cyclic			
6-member or more	1685-1665	s.	$\nu_{C=O}$
5-member	1724-1708	s.	$\nu_{C=O}$
α, β, α^1, β^1-unsaturated	1670-1663	s.	$\nu_{C=O}$

* Moreover, substituted benzenes have peaks characteristic of each substitution type in the 2000-1650 cm^{-1} band.

Table 1a, continued

Compound	Frequency (cm^{-1})	Intensity* (ε)	Notes
aryls	1700-1680	s.	$\nu_{C=O}$
diaryls	1670-1660	s.	$\nu_{C=O}$
α-diketones	1730-1710	s.	$\nu_{C=O}$
β-diketones (enol)	1640-1540	s.	$\nu_{C=O}$
1,4-quinone	1690-1660	s.	$\nu_{C=O}$
Aldehydes	2900-2820	w.	ν_{CH}
	2775-2700	w.	ν_{CH}
saturated aliphatic	1740-1720	s.	$\nu_{C=O}$
α, β-unsaturated aliphatic	1705-1680	s.	$\nu_{C=O}$
α, β, γ, δ-unsaturated aliphatic	1680-1660	s.	$\nu_{C=O}$
aromatic	1715-1695	s.	$\nu_{C=O}$.
	1670-1645	s.	There is a ν_{OH} band with intramolecular hydrogen bond
Esters and lactones			
saturated acyclic acetates	1750-1735	s.	$\nu_{C=O}$
	1060-1000	w.	Vibrations involving C—O bond
	1247-1236	s.	Vibrations involving C—O bond
formates	1200-1180	s.	
	1161-1152	m.	
propionates and higher esters	1200-1163	s.	
saturated cyclic δ-lactones	1750-1735	s.	$\nu_{C=O}$
γ-lactones	1780-1760	s.	$\nu_{C=O}$
β-lactones, unsaturated	~ 1820	s.	$\nu_{C=O}$
vinyl ester type	1800-1770	s.	There is a strong $\nu_{C=C}$ band at 1690-1650 cm^{-1}
α, β-unsaturated and aryls	1730-1717	s.	$\nu_{C=O}$

Table 1a, continued

Compound	Frequency (cm^{-1})	Intensity* (ε)	Notes
α β-unsaturated δ-lactones	1730-1717	s.	$\nu_{C=O}$
α, β-unsaturated γ lactones	1760-1740	s.	$\nu_{C=O}$
β, γ-unsaturated γ-lactones	1880	s.	$\nu_{C=O}$
α-keto esters	1755-1740	s.	$\nu_{C=O}$
β-keto esters (enol)	1735, ~ 1650	s.	β-ketone $\nu_{C=O}$ at ~1750 cm^{-1}. Wide, very strong C=C band at ~ 1630 cm^{-1}
	1310-1250	s.	Vibrations involving C—O bond
	1200-1100	s.	
Carboxylic acids			
saturated aliphatic	3550-3500	m.	ν_{OH}, free OH group
	3300-2500	w.	ν_{OH}, bound OH group
	1760	s.	$\nu_{C=O}$
α, β-unsaturated aliphatic	1715-1690	w.	$\nu_{C=O}$
	3500-2500	w.	ν_{OH}
aromatic	1700-1680	s.	$\nu_{C=O}$
	955-890	var.	Wide δ_{OH} band
Acid anhydrides			
saturated cyclic	1850-1800	s.	$\nu_{C=O}$
	1790-1740	s.	
α, β-unsaturated aromatic acyclic	1830-1780	s.	$\nu_{C=O}$
	1770-1720	s.	
saturated 5-member rings	1870-1820	s.	$\nu_{C=O}$
	1800-1750	s.	
α, β-unsaturated 5-member rings	1850-1800	s.	$\nu_{C=O}$
	1830-1780	s.	

Table 1a, continued

Compound	Frequency (cm^{-1})	Intensity* (ε)	Notes
Acid halides	1820-1785	s.	$\nu_{C=O}$
α, β-unsaturated	1780-1750	s.	$\nu_{C=O}$
aromatic	1750-1720	m.	$\nu_{C=O}$
Acid amides			
primary	3540-3480	s.	ν_{NH}, free
	3420-3380	s.	ν_{NH}, free
	3360-3320	m.	
	3220-3180	m.	
	~ 1650	s.	$\nu_{C=O}$, band "Amide I" for solid or concentrated solutions
	~ 1690	s.	$\nu_{C=O}$, for dilute solutions
	1620-1590	s.	δ_{NH} and ν_{C-N}, band "Amide II" for dilute solutions
	1420-1420	m.	Band "Amide III"
secondary	3440-3420	s.	ν_{NH}, free (*cis*)
	3460-3440	s.	ν_{NH}, free (*trans*)
	3180-3140	m.	ν_{NH}, bound (*cis*)
	3330-3270	m.	ν_{NH}, bound (*trans*)
	1680-1630	s.	$\nu_{C=O}$, "Amide I" for solid solutions
	1700-1665	s.	$\nu_{C=O}$ for dilute solutions
	1570-1515	s.	Band "Amide II" for solid solutions
	1550-1510	s.	Dilute solutions
	1305-1200	m.	"Amide III"
tertiary	1670-1630	s.	$\nu_{C=O}$, "Amide I" (solid or in solution)

Table 1a, continued

Compound	Frequency (cm^{-1})	Intensity* (ε)	Notes
Alcohols and phenols			
	3670-3590	var.	ν_{OH}, free (narrow band)
dimers	3550-3450	var.	ν_{OH}, bound (narrow band). Intensity decreases with dilution
polyassociates	3400-3200	s.	ν_{OH}, wide band. Intensity decreases with dilution
chelates	3200-2500	w.	ν_{OH}, bound, very wide band. No intensity change with dilution
primary	~ 1050	s.	ν_{C-O}
	1350-1260	s.	No practical significance (δ_{OH})
secondary	~ 1100	s.	
	1350-1260	s.	
tertiary	~ 1150	s.	
	1410-1310	s.	
phenols	1200	s.	
	1410-1310	s.	
C. Nitrogen-containing compounds			
Amines			
primary free	3500-3300	m. (~ 30)	Two bands, ν_{as} and $\nu_{s\ NH_2}$
	1650-1590	s.-m.	δ_{NH}
secondary free	3500-3310	m. (30-40)	ν_{NH}, one band
	1650-1550	w.	δ_{NH}
aromatic			
primary	1340-1250	s.	C—N stretching
secondary	1350-1280	s.	vibrations
tertiary	1360-1310	s.	
	1220-1020	w.	

Table 1a, continued

Compound	Frequency (cm^{-1})	Intensity* (ε)	Notes
Imines	3400-3300	m.	One band
	1690-1640	var.	$\nu_{C=N}$ band (1690-1640 cm^{-1})
Amine salts	3130-3030	m.	ν_{NH}
	1600-1575	s.	δ_{NH}
	~ 1500	m.	δ_{NH}
Amino acids			
NH_2-containing amino acids	3130-3030	m.	$\nu_{NH_3^+}$
	1660-1610	w.	$\delta_{NH_3^+}$, amino acid band I
	1550-1485	m.	$\delta_{NH_3^+}$, amino acid band II
dicarboxylic α-amino acids	1755-1720	s.	C=O vibrations of unionized carboxyl group
	1230-1215	s.	Vibrations involving C—O bond
	1600-1560	s.	Vibrations of ionic carboxyl grou
	2760-2530	w.	
	2140-2080	w.	
	1335-1300	m.	
Amino acid salts	3400-3200	s.	ν_{NH_2}
	1600-1560	s.	$\nu_{\overline{CO}_2}$
Alkyl nitriles			
saturated	2260-2240	m. (10-150)	$\nu_{C\equiv N}$
α, β-unsaturated	2235-2215	s.	$\nu_{C\equiv N}$
Aryyl nitriles	2240-2220	m.	$\nu_{C\equiv N}$
Isocyanates	2275-2240	m.	$\nu_{C\equiv N}$
Isocyanides	2220-2070	m.	$\nu_{C\equiv N}$

Table 1a, continued

Compound	Frequency (cm^{-1})	Intensity* (ε)	Notes
Azo compounds	1630-1575	var.	$\nu_{N=N}$
Nitro-compounds			
primary and secondary	1565-1545	s.(500 600)	ν_{as} NO_2
	1385-1360	s.(100 200)	ν_s NO_2
	~ 1380		
tertiary	1545-1530	s.	ν_{as} NO_2
	1360-1940	s.	ν_s NO_2
unsaturated	1530-1510	s. (500-700)	ν_{as} NO_2
	1360-1335	s. (200-1000)	ν_s NO_2
α-halide nitro compounds	1580-1570	s. (500-700)	ν_{as} NO_2
	1355-1340	s. (200-700)	ν_s NO_2
α-dihalide nitro-compounds	1600-1575	s.	ν_{as} NO_2
	1340-1325	s.	ν_s NO_2
aromatic	1570-1510	s. (300-800)	ν_{as} NO_2
	1370-1310	s. (100-900)	ν_s NO_2
hem-dinitro-compounds	1590-1580	s. (~ 900)	ν_{as} NO_2
	1343-1330	s.	ν_s NO_2
trinitro-compounds	1610-1590	s. (1200-1500)	ν_{as} NO_2
	1290-1305	s.	ν_s NO_2
tetranitro-compounds	1650-1620	s.	ν_{as} NO_2
	1280-1270	s.	ν_s NO_2
Nitrates	1650-1610	s.	ν_{as} NO_2
	1300-1255	s.	ν_s NO_2
Nitramines	1585-1530	s.	ν_{as} NO_2
saturated	1300-1260	s.	ν_s NO_2

Table 1a, continued

Compound	Frequency (cm^{-1})	Intensity* (ε)	Notes
	790-770	m.	
Nitrites			
trans-form	1680-1650	s.	$\nu_{N=O}$
	815-750	s.	Vibrations involving bond N—O
cis-form	1625-1610	s.	$\nu_{N=O}$
	850-810	s.	
D. Sulphur-containing compounds			
Sulfoxides	1070-1030	s.	$\nu_{S=O}$
Sulfones	1160-1140	s. (300-600)	ν_s SO_2
	1350-1300	s. (100-400)	ν_{as} SO_2
Sulfonamides	1180-1140	s.	ν_s SO_2
	1350-1300	s.	ν_{as} SO_2
Sulfonic acids	1260-1150	s.	ν_{as} SO_2
	1080-1010	s.	ν_s SO_2
	650	s.	
E. Phosphorus-containing compounds			
Phosphonates	1350-1150	s.	$\nu_{P=O}$
	1250-1150	s.	$\nu_{P=O}$ at hydrogen bond
G. Heterocyclic compounds			
Furans	3165-3125	s.	ν_{CH}
	1565	s.	Ring vibrations
	1500	s.	

Table 1a, concluded

Compound	Frequency (cm^{-1})	Intensity* (ε)	Notes
	1030-1045	s.	The most characteristic band of furans
	885-870	s.	
	800-740	s.	
Thiophenes	3125-3050		ν_{CH}
	~ 1520		Ring vibrations
	~ 1040		
	750-690	s.	The strongest band of thiophene
Pyrroles, indoles	3440-3400	m.	ν_{NH} in solutions
	~ 1565	var.	Ring vibrations
	~ 1500	var.	
Pyridines	3070-3020	s.	Stretching and deformation vibrations of CH
	900-670	s.	Ring vibrations
	1650-1580	m.	
	1580-1550	w.	
	1510-1480	m.	

TABLE 2a

CONSTANTS OF SUBSTITUENTS FOR CALCULATION OF PROTON CHEMICAL SHIFTS

Fundamental element (hypothetical methane) $T_0 = 0.824$
Element of carbon skeleton $-C^2$ $T_1 = +0.363$
Element of carbon skeleton $-C^2-C^3$ $T_2 = +0.296$
Element of carbon skeleton $-C^2(-C^3)_2$ $T_3 = +0.185$
Element of carbon skeleton $-C^2(-C^3)_3$ $T_4 = 0.184$

Substituent	Position	Constant	Substituent	Position	Constant
Double bond	1	$T_5 = +3.860$	$O-CO-CR_3$	2	$T_{15} = +0.135$
"	2	$T_6 = +0.689$	$O-CO-CR_3$	3	$T_{16} = +0.081$
"	3	$T_7 = 0.094$	$-Cl$	1	$T_{17} = +2.175$
Triple bond	1	$T_8 = +1.102$	$-Cl$	2	$T_{18} = +0.303$
Triple bond	2	$T_9 = +0.749$	$-Cl$	3	$T_{19} = +0.139$
$=O$	1	$T_{10} = +8.600$	$-Br$	1	$T_{20} = 2.144$
$=O$	2	$T_{11} = +0.986$	$-Br$	2	$T_{21} = 0.428$
$=O$	3	$T_{12} = -0.074$	$-Br$	3	$T_{22} = 0.070$
$-O-CH_3$	2	$T_{13} = -0.450$	$-I$	1	$T_{23} = 1.784$
$-O-CO-CR_3$	1	$T_{14} = +2.998$	$-I$	2	$T_{24} = 0.417$

TABLE 3a

INCREMENTS FOR CALCULATING CHEMICAL SHIFTS OF PROTONS AT THE DOUBLE BOND

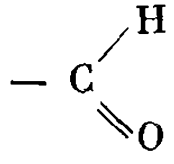
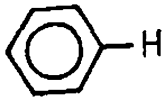
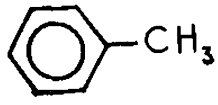
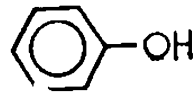
Substituent	δ, (ppm)		
	Z_{hem}	Z_{cis}	Z_{trans}
—Alkyl	0.45	−0.22	−0.28
$-CH_2O$	0.64	−0.01	−0.02
$-CH_2X$ (X—Cl, F, Br)	0.70	0.11	−0.04
—C=C, isolated	1.00	−0.09	−0.23
—C=C, conjugated	1.24	0.02	−0.05
—C=O, isolated	1.10	1.12	0.87
C=O, conjugated	1.06	0.91	0.74
	1.02	0.95	1.17
—Cl	1.08	0.18	1.17
—Br	1.07	0.45	0.55
—I	1.14	0.81	0.88

TABLE 4a

CHEMICAL SHIFTS OF PROTONS
(DILUTE SOLUTIONS IN CHLOROFORM)

Proton type[1]	δ[2]		Proton type	δ[2]	
	ppm	Hz[3]		ppm	Hz
$R-\mathbf{CH_3}$	0.9	54	$O=C-\mathbf{CH_3}$ (R)	2.3	126
$R-\mathbf{CH_2}-R$	1.3	78			
$R_3-\mathbf{CH}$	2.0	120			
$R_2C=\mathbf{CH_2}$	~ 5.0	300	$R-\mathbf{CH_2}-Cl$	3.7	220
$R_2C=\mathbf{CH}$ (R)	~ 5.3	320	$R-\mathbf{CH_2}-Br$	3.5	210
			$R-\mathbf{CH_2}-I$	3.2	190
	7.3	440	$RCH(Cl)_2$[4]	5.8	350
			$R-O-\mathbf{CH_3}$	3.8	220
$R-C\equiv C-\mathbf{H}$	2.5	150			
$R_2C=C-\mathbf{CH_3}$ (R)	~ 1.8	108	$(R-O)_2\mathbf{CH_2}$[4]	5.3	320
			$R-C(=O)-\mathbf{H}$	9.7	580
	2.3	140	$R-O-\mathbf{H}$	5[5]	300
$R-C(=O)-OH$	11	660[5]		7[5]	420

[1] The protons causing resonance absorption are shown by bold type. The group R is the saturated carbon chain.
[2] The reference compound is tetramethylsilane.
[3] The operational frequency of the spectrometer is 60 MHz.
[4] Sensitive to solvent, concentration and temperature.
[5] The shift due to two chlorine atoms or two RO-groups is larger (but by a factor less than 2) than the shift due to one Cl atom or RO-group.